THE SPECIALISTS' SERIES

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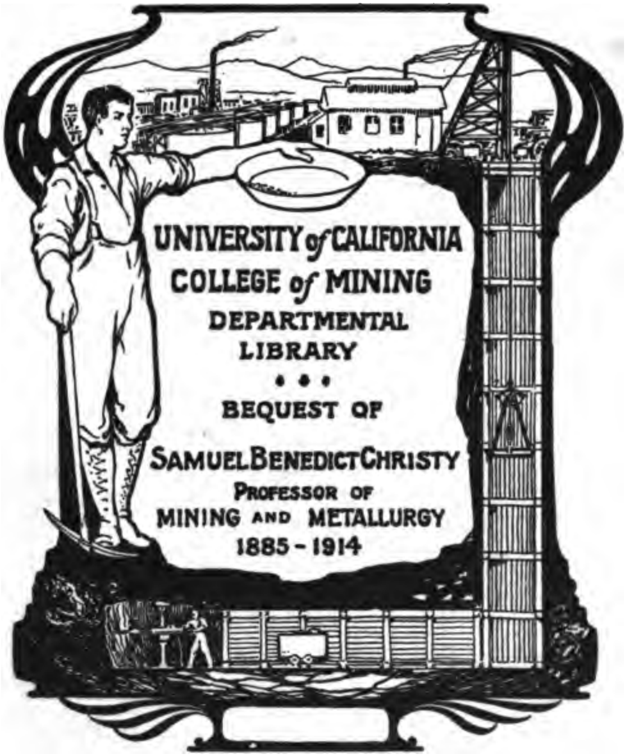

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STEEL WORKS ANALYSIS

THE SPECIALISTS' SERIES

STEEL WORKS ANALYSIS

BY

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SOMETIME CHIEF CHEMIST AT THE SHEFFIELD STEEL AND IRON WORKS

WHITTAKER AND CO.

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PREFACE

THIS little work has been written specially for assistants in steel works laboratories and students taking up the analytical chemistry of iron and steel with a view to becoming steel works chemists. The great object kept in view by the author has been to produce a *practical* book: he has therefore avoided compilation, and written from personal experience. The first essential in any analytical process is accuracy: when this can be combined with rapidity, well and good; but where speed is obtained at the expense of accuracy, the result is worse than useless, it is misleading. On the other hand, the appalling elaboration with which the authors of some text-books proceed to separate possible or impossible traces of rarely occurring elements from those invariably present, often defeats its own object, and together with a great loss of time, introduces errors far greater than those it is intended to avoid. It is to be regretted that the writers of books on iron and steel analysis usually deem it necessary to describe without comment every method—good, bad, and indifferent—which has ever been published, thus leaving the student in doubt as to which is really the best process to employ. The author has

described only methods which he has proved to be reliable, or in a few difficult cases approximate.

The scheme of the book will be found to be somewhat new, and, it is trusted, convenient. The practical operations are fully described in their proper order in distinct paragraphs. Then following each method is an article setting forth the theory of the reactions involved. It should always be borne in mind, that even when using the most accurate method, a conscientious attention to details and *cleanliness* are absolutely necessary to ensure an accurate result, whilst dirty, slovenly analysis is sure to go wrong and be detected sooner or later. As a guide to students, typical analyses of the materials herein dealt with are tabulated at the end of the book. The author cannot too strongly urge students to remember the fact that a steel chemist and an analytical machine who turns out so many estimations per day are two very different personalities. Analysts deficient in a thorough knowledge of elementary chemistry, physics, and mathematics, and the principles of qualitative analysis, can claim to rank only with skilled artisans: in chemical analysis the head and the hands should always work together. For this reason the theoretical side of the question has been somewhat fully dealt with; this many may regard as unnecessary, because students before taking up quantitative work are expected, as the result of a previous course of pure chemistry, to know all about the ordinary reactions of the metals. In this matter the author's experience of a large number of such students has led him to expect nothing, and he has seldom been disappointed. Even with students really well grounded in pure chemistry, the possession of knowledge

and the ability to apply it are two widely different things; also it should be remembered, that many of the separations of the metals described in text-books on qualitative analysis are exceedingly crude, and quite unfitted for accurate quantitative work. The author, it will be noticed, has mixed English and metric weights and measures, thus sacrificing scientific consistency on the altar of convenience. It is to be hoped, however, that before long the first-named system will be relegated to its proper place amongst the curiosities in the British Museum. It will be found that the author has sometimes criticized the errors of others, but he is nevertheless aware that a scientific book without mistakes would constitute something new under the sun, and he will regard as a favour the correction of any inaccurate statements contained herein. The author is indebted to his demonstrators, Mr. J. Jefferson and Mr. F. K. Knowles, for checking the accuracy of the calculations exemplified, and the strengths of the various volumetric solutions specified.

J. O. A.

The Technical School,
Sheffield, 1894.

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STEEL WORKS ANALYSIS

THE STEEL WORKS LABORATORY AND ITS APPLIANCES.

As the author has upon several occasions been requested to advise on the installation of a works laboratory, he has deemed it advisable to devote a brief article to the consideration of this subject. It will be assumed that the services of one analyst and a laboratory boy will be employed.

The Laboratory.

This should include two rooms, divided by a passage 5 ft. wide, namely, a small room, say 10 ft. sq. for the balance, and a larger room, say 20 ft. by 10 ft. for the laboratory itself. These rooms should be lofty, say 15 ft. high, and as far away as possible from steam-hammers, so as to avoid the effect of vibration on the balance. A ceiling sheathed with wood is desirable in the larger room, the possible falling of pieces of whitewash or plaster loosened by the action of acids is thus prevented. The benches should be of thoroughly seasoned non-resinous wood and stoutly built. That on which the balance is placed must be very rigid. The supply-tube for

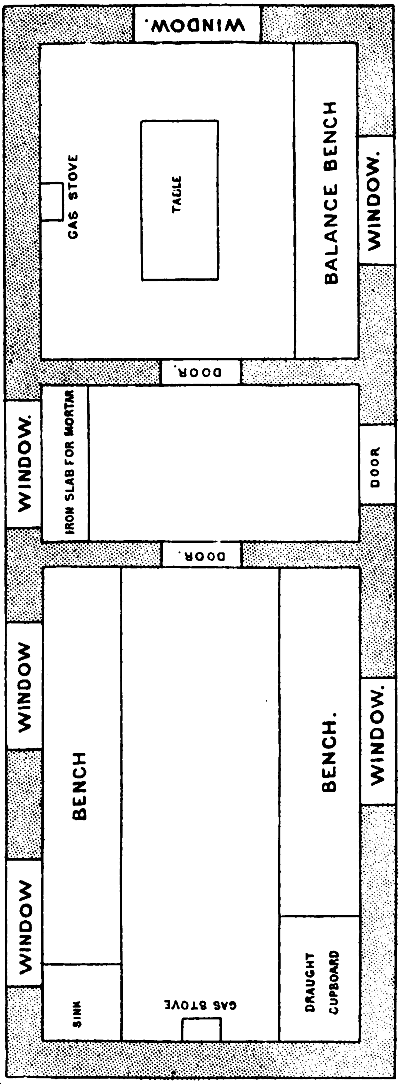


FIG. 1.

gas should be 2 in. in diameter, and the earthenware sink should be supplied with a tap connected with a good head of water if a filter-pump is to be used. To the main gas-pipe should be attached at least six Bunsen branches for $\frac{1}{2}$ in. rubber tubing; the taps for these branches are most convenient when placed under the bench, within easy reach of the hand. A draught cupboard of glass or white tiles is very desirable to carry off the more irritating fumes. In this must be at least two branches and taps for Bunsens; also a large, ordinary jet at the top of the cupboard to create a draught at the exit,—the latter should be of earthenware piping. The lower halves of the cupboard front

should slide in grooves, and be fastened in any desired position by means of strong wooden pegs placed in holes in the framework. Hinges or cords should not be used, as they are soon corroded by the action of acids. Both rooms will require numerous convenient shelves, drawers, and cupboards. A suggestive sketch of a plan of the laboratory thus briefly described will be seen in Fig. 1. The ventilation may be effected preferably through louvres on the ridge of the roof, or by means of swinging upper windows. Hot-water pipes or gas fires are best for heating the rooms, because they create no dust. In the passage, which much assists in isolating the balance from the fumes of the laboratory, should be a thick iron plate well supported by brick-work, and recessed for the reception of the steel mortar used for crushing hard alloys incapable of being drilled.

Analytical Appliances.

The balance.—Of these the balance is the most important item. In purchasing this it is true economy to buy a somewhat expensive instrument, that is to say, one provided throughout with agate or rock-crystal planes and knife edges. When the latter are in steel, they are sure sooner or later to corrode, and seriously impair the sensitiveness of the instrument. A *sine qua non* for steel works where analyses must be turned out quickly, is a rapid, short-beam balance; the length of beam should not exceed 8 inches. The supporting wires to which the pans are attached should be parallel, and sufficiently far apart to readily admit of the weighing of potash bulbs, etc. The pointer should be sensitive to $\frac{1}{10000}$th of a gramme. For steel works use the author has found the 8-in. beam

balance, with round pans, made by Oertling, a sound and reliable instrument at a moderate price. For use with this a set of weights from 50 grammes downwards will be found convenient. The interior of the balance-case should always be kept dry by the presence of several little pots of strong commercial sulphuric acid. These, however, should be only half full, and require watching, otherwise the absorbed moisture will fill up the pot and run over. In fact, it is advisable to wash out and dry the jars and replenish them with strong acid about once a month.

Weighings should never be made directly on the balance-pan, but on a sufficiently large and conveniently bent slip of aluminium foil; the latter is carefully counterpoised on the other pan by means of a little piece of lead.

The analytical balance should never be employed for weighing out large quantities of re-agents: a comparatively coarse pair of scales should be used for such purposes.

The gas-muffle furnace.—One of these is almost indispensable to accurate working. It should be fitted with a "salamander" muffle, which, though somewhat expensive so far as first cost is concerned, is really an economy, as it lasts out two or three ordinary clay muffles. When lighting the furnace, withdraw the muffle, throw a burning wax-match on the iron burners, turn on the gas, and replace the muffle.

Heating plates.—These are of cast-iron ¼ in. in thickness; four of them will be found convenient, namely, two 12″×12″, one 12″×24″ (for the draught cupboard), and one 9″×9″ (for the carbon bath). The plates are supported on quadrupods, and heated by Bunsen burners placed underneath them.

Bunsen burners.—The small tubes at the bottom of these lamps require removing in order to get a flame of large

volume, which spreads over a considerable area in the middle of the heating-plate. In order to obtain the maximum heat, the plates usually require lowering well into the Bunsen flame by cutting shorter the legs of the quadrupod.

Water bath.—This consists of a somewhat deep cast-iron vessel enamelled inside, and provided with a series of copper rings, which support evaporating dishes of various sizes over the boiling water.

Air bath.—This is of copper, and the supply of gas to the small Bunsen burner by which it is heated is adjusted by means of a Reichardt's mercury regulator, so that the temperature of the shelf is always about 100° C. By a little preliminary attention to the screw and thermometer till the right position is obtained, a steady temperature ranging not more than one degree on either side of 100 is readily ensured.

Foot blow-pipe.—This is useful for fusions requiring a high temperature, such as are necessary in the analysis of fire-bricks, etc.

Filter pump.—Where a good head of water is available, one of the very cheap but effective glass pumps now obtainable is often useful. It requires fitting over the sink into which the waste-pipe runs. The exhausting tube may be led round to the bench, where it is attached to the side tube of a strong, conical filter vessel. The india-rubber stopper of the latter carries a plain 2¼ in. funnel, in the apex of which must be placed a perforated platinum cone.

The foregoing apparatus requires to be used with judgment; many precipitates filter so rapidly as to render its employment unnecessary. For finely-divided precipitates such as $BaSO_4$ and WO_3 it should never be used. But

in the case of slimy, slow-filtering precipitates, such as that obtained from ammonium acetate in the combined molybdate and magnesia process for estimating phosphorus, the pump is of great value in saving time.

Flasks.—For most purposes, the ordinary, nearly globular flask serves very well, but for precipitation purposes a vessel designed by Mr. J. Taylor, and known as the registered flask, is most suitable. In form it is a cone with a radiused bottom, so that every part of the vessel can be reached by the "policeman" used for detaching adhering precipitate from the sides. Watch-glasses serve well for flask covers.

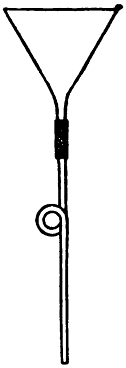


FIG. 2.

Beakers.—These are convenient in two designs, namely, the lipped conical beaker (used chiefly for the reception of useless filtrates), and the wide form with spout. (*In the following pages, when the term beaker is used, unless otherwise specified, the latter form is referred to.*) Concave clock-glasses, rather larger in diameter than the vessel itself, form the handiest covers for beakers.

Funnels.—These are, as a rule, best ribbed, but for finely-divided precipitates, such as $BaSO_4$, a plain funnel is safest. It is also sometimes advisable in such cases to cut off the stem of the funnel about half an inch from the apex: this of course renders the filtration slower, whilst a looped glass tube attached to the stem by india-rubber tubing (Fig. 2) considerably increases the rate of flow.

It is important that all funnels should have the correct angle, namely 60°, so that the circular filter-papers will fit perfectly.

Funnel hangers.—These useful little articles may be bent out of thin glass rods; they are made as follows: six inches of $\frac{1}{8}''$ diameter glass rod is heated in the middle, and bent with a radius of $\frac{3}{8}''$ to an angle of 180°. Each limb of the hanger is then heated two inches from the end, and bent sharply to an angle of 105°: the hanger is placed on the edge of the beaker with the radius inside, and in this the funnel is supported (Fig. 3).

Filter-driers.—These consist of glazed earthenware cylinders $\frac{1}{8}''$ thick, 2″ high, by $1\frac{1}{2}''$ inside diameter. Filters containing the washed precipitate are removed from the funnel, and placed in the drier on the hot plate to dry before ignition. The cylinders also serve to support the covers, placed concave side downward, of beakers, the contents of which are evaporating on the plate.

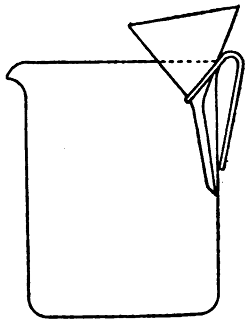


FIG. 3.

Desiccators.—These should have the ground surfaces slightly greased to render them air-tight. In the bottoms layers of pumice stone in rough pieces about $\frac{1}{2}$ in. square are half-covered with strong sulphuric acid. Crucibles placed in the vessels to cool are best supported in a well-fitted pipe-stem triangle.

Wash bottles.—For general use a 40-oz. flask with a jet of medium fineness will be found most convenient. In addition to two such large flasks (one for hot and the other for cold water) it is also advisable to fit up two or three 12-oz. flasks for special washing liquids, *e.g.* 2 % nitric acid. One or two straight-shooting jets of fine bore should be made and treasured like old gold; they are

invaluable for washing precipitates, such as the yellow phosphorus compound, off the filter-paper, and also for washing small and possibly slightly soluble precipitates, for which only such a volume of washing liquid as is absolutely necessary should be used.

Filter-papers.—For collecting precipitates to be weighed ashless papers (which have been washed free from iron with HCl, and from silica with HF) should be used. They may be purchased in packets of three convenient sizes, namely, 90 mm., 110 mm., and 125 mm. diameter, corresponding respectively to 2″, $2\frac{1}{4}$″, and 3″ funnels. The smaller size should also be obtained in two degrees of rapidity; the slow, close-grained filter being used for finely-divided precipitates like $BaSO_4$. For ordinary purposes the cheaper thick white German paper sold in sheets should be employed, and cut to size as required. For use in estimating manganese, circles $9\frac{1}{4}$″ diameter are requisite, which may be cut out by folding pieces of paper about 10″ sq. into four, and then cutting out the circle round a brass quadrant of $4\frac{5}{8}$″ radius and $\frac{1}{16}$″ thick. For collecting precipitates which have to be washed off the paper, 90 mm. diameter circles of hardened parchment-like surface will be found very convenient. Quick-filtering papers of this description can now be purchased in packets.

PRICED LISTS OF APPARATUS AND CHEMICAL RE-AGENTS REQUIRED.

THE following estimate provides apparatus and chemicals for carrying out all the analyses dealt with in this book. These lists can of course be much reduced when only a limited range of work is required.

APPARATUS.

	£	s.	d.
1 balance with 8-in. beam	13	13	0
1 set of weights—50 grammes to 1 milligramme ...	1	15	0
¼ oz. aluminium foil		1	0
1 specific gravity bottle—50 grammes		3	0
1 pair lb. scales for rough weighings		15	0
1 4-in. steel spatula			9
2 glass desiccators		5	0
1 pair platinum-tipped crucible tongs		12	6
1 covered platinum dish, 3″ diameter, 1½″ deep, weight about 45 grammes; 1 covered platinum crucible, 1¼″ diameter, 1½″ deep, weight about 27 grammes	6	0	0
3 covered porcelain crucibles, 2″ diameter		1	6
1 porcelain dish, 8½″ diameter		2	9
1 „ „ 6″ diameter		1	9
3 „ „ 2¾″ diameter		1	0
1 set of apparatus for estimation of carbon by combustion complete with furnace	8	0	0
7 lbs. combustion tubing		9	4
1 gas furnace with salamander muffle	2	15	0
3 large Bunsen burners		7	6
1 small „ „		1	3
1 gas blow-pipe with foot blower	1	8	6
1 air-bath with Reichardt's regulator	1	10	0
1 deep-water bath with concentric copper rings ...		9	6
1 set of apparatus for the volumetric estimation of sulphur complete with duplicate tubes...	4	4	0
1 graduated bromine absorption-tube with stopper and side tap, for estimation of sulphur		10	0
	£43	7	4

	£	s.	d
Brought forward ...	43	7	4
1 20-oz. cylindrical measuring glass		3	6
2 sets of cylindrical measures, 100, 50, and 10 cc. ...		7	2
1 set of graduated flasks, 1000, 500, 250, 120, 100, 90, 60, 50, 605, 301, and 75 cc.		10	0
1 set of graduated pipettes, 1, 2, 5, 10, 15, 50, and 100 cc.		3	10
2 graduated burettes, 50 cc., divided in 10ths, with glass taps		10	6
1 graduated burette, 20 cc., divided in 10ths		3	6
2 hydrometers, 900 to 1000, and 1000 to 1300		5	0
1 pair graduated carbon tubes, 12 cc., graduated in 10ths		5	0
1 pair ditto, 20 cc., graduated in half cc.		5	0
1 carbon bath complete with cover, tubes, and rubber rings		10	6
4 quadrupod stands, $8\frac{1}{4}''$ sq.		16	0
2 " " $6\frac{1}{4}''$ sq.		6	0
1 tripod stand, $4\frac{1}{4}''$ side			10
1 iron plate, $24'' \times 12''$ ... ... }			
2 " " $12'' \times 12''$ ... ... }		3	6
1 " " $9'' \times 9''$ ... ... }			
1 agate mortar and pestle, $2\frac{3}{4}''$ diameter		12	0
1 Wedgwood ware mortar and pestle, $6\frac{1}{2}''$ diameter ...		3	0
1 steel crushing mortar in three pieces		16	0
1 set of tin sieves, 30, 60, and 90 meshes per in. ...		5	0
2 7-in. perforated sieves with holes respectively $\frac{3}{32}$ and $\frac{1}{8}$ in. diameter		5	0
3 burette stands		13	6
1 universal wooden retort stand		7	6
2 test tube stands		1	2
3 30-oz. flasks		3	0
3 20-oz. "		2	6
3 10-oz. "		2	0
6 6-oz. "		3	0
3 30-oz. registered flasks		3	6
1 80-oz. beaker		1	6
3 40-oz. "		3	6
12 20-oz. "		10	0
5 5-oz. "		1	3
6 14-oz. conical beakers		5	0
1 set of beaker covers, four 4-in., six 5-in., three 6-in., and one 9-inch		5	4
1 dozen assorted watch-glasses		1	6
2 2-in. ribbed funnels			8
3 $2\frac{1}{4}$-in. " "		1	3
2 3-in. " "		1	0
	£53	5	10

	£	s.	d.
Brought forward ...	53	5	10
2 $4\frac{3}{4}$-in. ribbed funnels		1	6
2 1-in. plain funnels			6
2 $2\frac{1}{4}$-in. „ „			10
1 dozen test tubes, $6'' \times \frac{1}{2}''$			6
$\frac{1}{2}$ „ „ $6'' \times \frac{5}{8}''$			5
$\frac{1}{2}$ „ „ $6'' \times 1''$			6
3 glass cylinders, $8'' \times 1\frac{3}{4}''$, for washing gases		2	6
2 8-oz. hard glass oxygen flasks		1	4
1 glass filter-pump		2	6
1 platinum cone		7	6
2 stout glass conical filter-pump flasks with side tubes		4	0
2 200° C. thermometers, milk glass scale, enclosed tube		5	0
6 yards red india-rubber Bunsen tubing		6	9
1 yard thick walled black india-rubber tubing		1	0
1 yard red india-rubber tubing, $\frac{1}{4}''$ diameter		1	0
1 set assorted india-rubber bungs		10	0
1 set brass cork borers		3	0
2 sq. glazed white tiles		1	0
1 6-in. saw file		1	0
1 6-in. rat-tailed file		1	0
2 lbs. assorted glass rod and tubing		2	6
6 covered clay crucibles, $3\frac{3}{8}''$ high		1	0
1 set of apparatus for gas analysis complete with batteries, induction coil, and 10 lbs. of mercury	8	15	0
1 Kipps' sulphuretted hydrogen apparatus with bulb 6″ diameter	1	0	0
1 dozen earthenware glazed cylinders, $1\frac{1}{2}''$ inside diameter, $\frac{1}{8}''$ thick, by 2″ high		3	0
1 dozen assorted pipe-stem triangles		3	0

BOTTLES.

	£	s.	d.
1 set of 20-oz. narrow-mouth stoppered bottles with sand blast labels as follows—Sulphuric Acid, Hydrochloric Acid, Nitric Acid, Nitric Acid 1·20, Aqua Regia, Acetic Acid, Sulphurous Acid, Ammonium Acetate, Ammonium Hydrate, Ammonium Molybdate, Ammonium Oxalate, Barium Chloride, Sodium Acetate, Sodium Phosphate	1	3	6
1 6-oz. narrow-mouth stoppered bottle with sand-blast label—Bromine		1	0
5 2-oz. ether stoppered and capped bottles for preserving standard steel drillings		7	6
	£67	14	2

	£	s.	d.
Brought forward ...	67	14	2
6 8-oz. narrow-mouth plain stoppered bottles		3	0
1 dozen 1-oz. wide-mouth stoppered sample bottles ...		3	0
Winchester quarts and sundry bottles for holding stock re-agents	1	0	0

CHEMICALS.

	£	s.	d.
2 Winchesters pure hydrochloric acid		6	0
2 „ „ nitric „		9	0
2 „ „ acetic PB „		5	0
1 „ „ sulphuric „		4	3
1 syphon liquid sulphurous anhydride	1	0	0
1 lb. molybdic acid (pure)		5	6
1 oz. crystal chromic acid „			4
2 oz. hydrofluoric „ „			8
2 oz. oleic acid „			4
1 lb. bromine „		3	0
1 lb. ammonium chloride „		1	0
1 lb. „ carbonate „		1	6
1 lb. „ oxalate „		2	0
4 oz. „ molybdate „		2	0
2 oz. „ phosphate (pure)			5
1 lb. Potassium nitrate „			9
1 lb. „ hydrate (stick)		1	3
1 oz. „ ferricyanide (pure)			4
1 oz. „ (or ammonium) sulphocyanide		1	0
2 oz. „ permanganate (pure)			4
2 oz. „ iodide „		2	0
1 lb. „ carbonate „		1	9
1 lb. „ bichromate „		1	6
1 lb. „ chlorate „			8
½ lb. Sodium phosphate „			5
1 lb. „ acetate „			8
2 lbs. „ carbonate „		1	8
1 lb. „ hyposulphite „			8
1 lb. „ hydrate (stick)		1	3
8 oz. „ hydrate from sodium		6	3
1 lb. barium chloride (pure)			8
½ lb. magnesium chloride (pure)			6
2 lbs. calcium chloride		1	8
2 lbs. cupric chloride (pure)		5	0
[1] 1 lb. granular oxide of copper (pure)		4	0
	£73	13	6

[1] Twelve ounces of electrotype copper foil for conversion into oxide by ignition may be substituted for this item. (See p. 30.)

	£	s.	d.
Brought forward ...	73	13	6
1 lb. ferrous sulphate (pure)			4
4 oz. pure chromate of lead			9
2 lbs. ferrous sulphide			10
1 lb. white marble			3
2 lbs. granulated zinc		1	0
1 lb. pure oxide of magnesium		1	6
½ lb. „ precipitated chalk		1	0
4 oz. re-crystallized acetate of lead			8
2 oz. citric acid			4
2 oz. pure silver nitrate		2	0
1 dram phenol-phtalein			6
¼ oz. methyl orange			6
1 box each red and blue litmus papers		2	6
2 oz. electrotype copper			6
½ lb. Italian asbestos		5	0
½ lb. alchol (rectified spirit)		1	0
2 oz. wheat starch			2
3 lbs. pumice stone		1	6
2 lbs. white sand			2
12 gallons distilled water		3	6

FILTER PAPERS.

	£	s.	d.
100 chemically pure circles (No. 589), 90 mm. diameter		2	8
100 „ „ „ 110 „ „ ...		3	2
100 „ „ „ 125 „ „ ...		3	6
100 „ „ „ (hardened) 90 „ „ ...		2	9
2 quires thick German paper		5	0
Total	75	14	7
Less discount for cash, say 7½ %	5	15	0
Net cost	£69	19	7

CLASSIFICATION OF STEEL WORKS ANALYSIS.

A STEEL works analyst may be called upon to report upon the following materials :—

SECTION I.

METALS.

1. Wrought iron.
2. Steel.
3. Pig-iron.
4. Spiegel and ferro-manganese.
5. Ferro-chrome.
6. Ferro-silicon.
7. Ferro-aluminium and aluminium metal.
8. Ferro-tungsten and tungsten metal.
9. Ferro-nickel and metallic nickel.

SECTION II.

ORES.

10. Iron ores.
11. Manganese ores.
12. Chrome iron ore (Chromite).
13. Tungsten ore (Wolfram).

SECTION III.

REFRACTORY MATERIALS.

14. Acid furnace linings—
    (*a*) Ganister, silica bricks and sand.
    (*b*) Ordinary fire-bricks and clays.
15. Basic furnace linings—
    (*a*) Bauxite and Chromite.
    (*b*) Lime and magnesia bricks.
    (*c*) Dolomitic limestones.

SECTION IV.

FUELS.

16. Coal and coke.
17. Producer gases.

SECTION V.

SUNDRIES.

18. Slags.
19. Boiler water.

SECTION I. METALS.

ANALYSIS OF STEEL AND WROUGHT IRON.

As far as chemical constitution is concerned, these two products are not separated by any well-defined line of division, so that the same series of analytical operations serve as a rule for both; but it must be remembered that a distinction exists between the two in the fact that steel (except puddled, shear, and blister steels) has always been submitted to complete fusion and is thus practically free from involved slag. Wrought iron, puddled, blister, and shear steels have, however, never got beyond a pasty state of semi-fusion, and have in consequence more or less slag mechanically mixed with their structure.[1]

Steel always contains more or less of the following elements in addition to iron:—carbon, silicon, manganese, sulphur, and phosphorus; the determination of these elements constitutes an ordinary complete analysis. Besides these constituents, there may be present by design or accident the following:—tungsten, chromium, aluminium, nickel, copper, arsenic, and it is alleged titanium. The author has never yet met with *steel* containing the last-mentioned element in more than mere traces.

[1] No satisfactory method has at present been found to accurately separate the constituents of the slag from those actually alloyed with the iron.

In addition to these elements, steel contains the gaseous bodies hydrogen [1] and nitrogen, and sometimes oxygen : the last probably exists as dissolved ferrous oxide; it is not definitely known whether the two first-named gases are combined with or merely occluded in the iron.

For the determination of hydrogen and oxygen reliable and satisfactory methods have yet to be found.[2] Professor Ledebur has made some determinations of oxygen as water by heating steel drillings to redness for several hours in a current of pure dry hydrogen, and the author (see page 215) has attempted to estimate the hydrogen as water by combusting the steel in drillings in pure oxygen; but owing to the elaborate precautions necessary, both methods are tedious, and the results at best of dubious value.

Mr. A. H. Allen has devised a method for the determination of the nitrogen present in steel as ammonia by means of the Nessler test,[3] but unfortunately, as far as is known, the determination of the minute percentage of this gas present is of small importance from a practical point of

[1] See important research by Mr. J. Parry, *Journal of Iron and Steel Inst.*, 1881, Part I., p. 189; and experiment by author, *Proceedings of Inst. Mechanical Engineers*, April 1893, p. 158.

[2] Mr. J. Parry has proposed a method for the estimation of the oxygen which he alleges to exist in steel as Fe_3O_4. The process consists in dissolving the steel at a gentle heat in a saturated solution of bichromate of potash, containing one-sixth its volume of strong sulphuric acid. The residue is filtered off, washed with water, then with potash solution to remove silica, and finally with water. It is dried, ignited, and weighed, the result being calculated to Fe_3O_4.

By this method it is possible in annealed high carbon steel to find 1 % of oxide of iron *when that compound is not present.* The residue consists not of Fe_3O_4, but of some undecomposed carbide of iron (of which in tool steel about 15 % exists), from which on ignition the carbon burns off, leaving the iron as Fe_2O_3.

[3] *Chemical News*, vol. xli., p. 231.

view. The steel chemist should not, however, ignore the smallest fact connected with the study of the marvellously complex material he is called upon to examine. Of all the elements connected with steel, carbon is by far the most important: as the blood is the life, so is the carbon the steel. This element may exist in iron in at least three forms—(*a*) graphite, or scales of free carbon mechanically mixed up with the structure of the metal. This form separates in steel high in carbon under certain abnormal conditions of rolling or annealing. (*b*) Combined carbon exists as a carbide of iron, which the researches of Abel[1] and Müller[2] indicate to possess the formula Fe_3C, or approximately it contains 93·3 % of iron and 6·7 % of carbon. Generally speaking, the carbon in normal steels exists almost entirely as this modification, chiefly in the form of metallic scales. Sometimes, however, it is more or less diffused in a fine state of division. (*c*) Hardening carbon. This is found in hardened steel. When such steel is polished, and treated with very dilute nitric acid, it is seen as a dark velvety powder upon the surface of the metal. It is probably more loosely associated with the iron than the combined (or cement) carbon, and is possibly merely a solution of carbon in iron. (Since writing the above a systematic research by the author and A. A. Read, published in the *Journal of the Chemical Society* for August 1894, has amplified and somewhat modified the above statements.)

The Estimation of Total Carbon by Combustion.

This process gives the total carbon present irrespective of its form of existence.

[1] *Proceedings of the Institute of Mechanical Engineers*, 1885.

[2] *Stahl und Eisen*, No. 5.

The determination of carbon by combustion is the most important operation the steel chemist has to undertake, because upon its accuracy depends the value of the indispensable and rapidly made colour tests to be described later on. The author will therefore deal with the matter very thoroughly, incorporating in this article a research which off and on has occupied several years.

Numerous methods have been proposed from time to time for the gravimetric estimation of carbon in steel, but only those processes are worthy of consideration which involve, first, the separation of the carbon from the steel in a solid form; secondly, its subsequent combustion with oxygen; and thirdly, the weighing of the resulting CO_2 after absorption in caustic potash. The method of direct combustion of the metal may be dismissed as quite out of the running, so far as steel is concerned. It requires the material treated to be in the state of an impalpable powder, a condition obviously impossible in most steels.

The liberation of the carbon from the steel may be effected in three ways—(*a*) by the action of weak hydrochloric acid and a galvanic current on a small bar of the steel (Binks and Weyl); (*b*) by the action of gaseous chlorine on steel drillings at a low red heat (Wohler); (*c*) by the action on steel drillings of a solution of cupric chloride or sulphate. The combustion of the impure residue, consisting chiefly of carbon, may be effected, first, by dry combustion at a red heat with oxygen; secondly, by moist combustion at a comparatively low temperature with sulphuric and chromic acids (Ulgren).

The author will now proceed to describe the results obtained in the research he carried out to determine the comparative accuracy of the methods just enumerated.

Preparation of the Standard Steel.

In order to obtain for the experiments an ample supply of homogeneous material, an acid Bessemer ingot 14 in. square was selected, and hammered down to blooms 6 in. square; the centre bloom was then taken and rolled into a billet 3 in. square. From the centre of this billet a bar 2 ft. long by 2 in. square was planed. From this bar, in the different parts of which no variation of carbon could be detected by the colour test, all the bars and drillings used in the research were taken.

It may here be remarked, once and for all, that all samples of steel or iron used for analysis should consist of drillings or turnings obtained with a dry tool, the use of oil or water being strictly prohibited, also that analyses made on filings are of very little value, because the sample is certain to be more or less contaminated with fragments of the file teeth.

Liberation of the Carbon by Galvanic Current.

The apparatus used consisted of a wide 16-oz. lipped beaker, in which was placed a flat porous cell containing a thin plate of platinum. The current was generated from a single pint Bunsen cell; the acid used in estimations 1 to 4 inclusive was made by adding 20 cc. of strong HCl solution to 350 cc. of distilled water. In estimation No. 5, a mixture of 35 cc. of acid and 350 cc. water were employed. The steel bars used were $\frac{1}{4}$ in. square by 2 in. long; about one-third of the weighed bar was immersed in the acidified water. The steel was suspended from a binding-screw, the latter being coupled by a stout brass wire to the carbon pole; the platinum plate was connected in a similar manner to the zinc of the battery. The action was con-

tinued for eighteen hours, when the stream of ferrous chloride falling through the liquid had almost ceased to descend. Then the carbonaceous residue, which to some extent retained the form of the original steel, was detached from the undissolved portion of the bar, and the latter was carefully cleaned into the beaker, dried and weighed, the difference between the first and second weighings of course representing the weight of metal taken. The porous cell served to prevent some carbonaceous particles (which often detached themselves from the main mass of spongy residue) reaching the platinum, where they might have been converted into gaseous hydrocarbons by the action of the (nascent) hydrogen, copiously evolved from the plate during the operation. It is unfortunately impossible to avoid a slight but continuous evolution of hydrocarbons from the iron pole whilst the dissolution is proceeding. This of course involves a slight loss of carbon, which error is gravely increased if the suggestion found in some text-books, of placing a piece of steel in a platinum basket, is carried out. It is therefore evident that this process is inapplicable to drillings, etc., a fact which in itself places it out of court as a generally practicable steel works method. The porous cell having been removed from the beaker and washed, the residue was filtered off, washed, dried, and burnt in oxygen in a manner to be described later on in connection with the method finally adopted by the author for the determination of carbon by combustion (see p. 29).

The main reaction involved in the above process is very simple, and may be formulated thus—

$$Fe + 2\ HCl = FeCl_2 + H_2$$

Iron and hydrogen chloride yield ferrous chloride, which remains in solution, and hydrogen, which is liberated in

bubbles at the platinum plate. The carbon is left in the first instance as carbide of iron; some of this, however, may decompose with the formation of chloride of iron, hydrocarbon gases, and free carbon; the spongy residue then consisting of a mixture of carbon and carbide of iron containing some combined water, and usually mixed with small amounts of other impurities. The results obtained by liberating the carbon by the foregoing method and burning the residue in oxygen will be found in the following table:—

Experiment No.	Weight of Steel taken.	Weight of CO_2 obtained.	Carbon per cent.
1	4·5652	0·0778	0·465
2	3·3522	0·0588	0·478
3	3·6999	0·0628	0·463
4	5·7453	0·0919	0·436
5	6·9287	0·1151	0·453
Mean	4·8583	0·0813	0·459
Greatest difference 0·042 % carbon.			

Liberation of the Carbon by Chlorine Gas.

The experiments with this process were made on very small drillings. The weights taken ranged from 2 to 2½ grammes, the last-named weight being the highest which could be conveniently employed. If, for instance, 3 grammes were used, it was found that the bulky mass of ferric chloride crystals formed was very liable to block up the exit-tube. The drillings were weighed out into a porcelain boat, the latter was placed in a glass combustion-tube lying in a Hoffman furnace. In one end of the tube was an india-rubber stopper carrying a glass exit-tube ⅛ in.

internal diameter leading into the open air. The other end of the combustion-tube was connected with the apparatus for generating and drying the chlorine. The latter was produced in a large flask (supported on a sand-bath) from 250 grammes of granulated manganese dioxide well covered with pure fuming HCl solution. By judicious manipulation of the heat, a prolonged and steady stream of gas was obtained. The chlorine was washed by passing it through two tall narrow cylinders containing water; it was then dried by passing (*a*) through a Meisterlich bulb charged with strong sulphuric acid, (*b*) through a large U tube closely packed with granulated pumice stone saturated with strong sulphuric acid, (*c*) through a Geissler bulb containing strong sulphuric acid. The chlorine was passed through the cold tube until it was certain that the whole apparatus was free from air; the boat containing the steel was then gently raised to a dull red heat, which was continued till the vapour of ferric chloride was no longer given off. This compound condenses in front of the boat in a heap of beautiful ruddy crystals. The current of gas was sufficiently rapid to prevent any chloride condensing behind the boat. The furnace was turned out, and the boat with its contents of finely-divided velvet-black carbon (mixed with manganous chloride, etc.) was allowed to cool in a gentle current of chlorine. It was then removed, and the carbon was converted into CO_2 in an apparatus to be afterwards described (Fig. 7). It was noticed that a few particles of the finely-divided carbon were sometimes present in the ferric chloride, being carried forward out of the boat by the gaseous stream. The india-rubber connections of the apparatus were much acted upon, and some of them required renewal during the experiments. The process

is an exceedingly disagreeable one, the chlorine unavoidably escaping during the removal of the boat, and the renewal of the re-agents for preparing the gas being very irritating to the lungs. The reaction involved in this process is thus formulated—

$$Fe + 3\,Cl = FeCl_3$$

Iron and chlorine yield ferric chloride: the residual carbon is not pure, having mixed with it the manganese present in the steel in the form of non-volatile manganous chloride. The results obtained are summarized in the following table:—

No. of Experiment.	Weight of Steel taken for analysis.	Weight of CO_2 obtained.	% Carbon.
1	2·25	0·0371	0·450
2	2·00	0·0321	0·438
3	2·25	0·0407	0·493
4	2·50	0·0418	0·456
5	2·00	0·0375	0·511
Mean	2·20	0·0378	0·470
Greatest difference, 0·073 % C.			

In experiment No. 1 some particles of carbon were noticed amongst the ferric chloride but were ignored. In estimation No. 2 the chloride appeared quite free from carbon. The ferric chloride in determinations 3, 4, and 5 was dissolved in water, any suspended particles of carbon were collected on recently ignited asbestos plugs, the latter, after washing and drying, were ignited in oxygen with their respective boats.

It will be noted that in carrying out this series of experiments, no special precautions were adopted to prevent any free or combined chlorine present in the carbonaceous residue passing forward to the potash bulbs, and

yet the mean result is somewhat low. The author, however, has reason to believe that any chlorine given off remained in the combustion-tube as cuprous chloride (see p. 40).

Moist Combustion Process.

The carbonaceous residues treated in the following experiments were obtained exactly as described in the cupric chloride method hereinafter recommended by the author as most convenient and accurate for the estimation of carbon by combustion (p. 29).

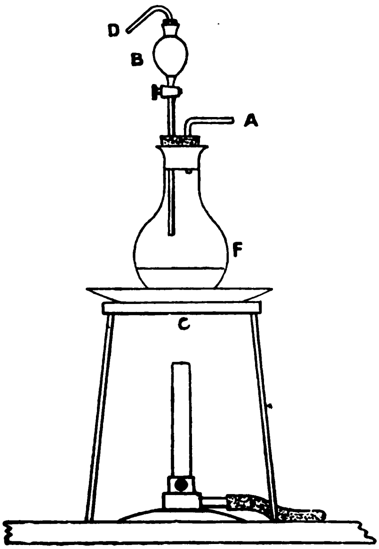


Fig. 4.

The washed moist asbestos plug on which the carbon had been collected was transferred to a wide 8-oz. flask F (Fig. 4), fitted with a rubber stopper carrying an exit bend A and a stoppered funnel B, the latter also fitted with a small rubber stopper and glass bend. To the plug was then added $7\frac{1}{2}$ grammes of chromic acid dissolved in 15 cc. of water, the stopper was inserted, and 50 cc. of strong H_2SO_4 were introduced into the funnel, which was then closed with its stopper. The flask was next placed on the sand-bath C, the bends A and D were then respectively connected by means of thick-walled tubing to the bulb E

and the tube C, Fig. 7, the flask and sand-bath, in fact, taking the place of the combustion-tube and furnace in the dry combustion apparatus. After weighing and replacing the absorption-tubes G and H, the tap of the funnel was opened till the 50 cc. of H_2SO_4 had run into the flask, this process, if necessary, being assisted by the aspirator J. After closing the top of the funnel gentle heat was applied to the mixture of carbon and chromic and sulphuric acids, the heating was continued until the mass turned green and semi-solid from the formation of chromic sulphate, and white fumes began to appear in the flask. It was found necessary to go to this stage to ensure the complete oxidation of the carbon. The Bunsen was turned out, and two litres of air were aspirated through the flask from the gas-holder. The absorption-tubes were then re-weighed to determine the weight of the CO_2 evolved. The reactions in this process may be formulated as follows—

$$6\,H_2SO_4 + 4\,CrO_3 + 3\,C = 3\,CO_2 + 2\,Cr_2(SO_4)_3 + 6\,H_2O$$

The author has observed in carrying out this process, that sometimes the fumes of SO_3 assume a peculiar physical condition in which they are not condensed in the sulphuric acid drying bulbs, and even to some extent pass the potash tubes. The results obtained by moist combustion are usually somewhat low, as will presently be seen, unless, as is often the case, no blank determination is made on the re-agents used. In the present set of experiments a washed plug 15 cc. of the chromic acid solution and 50 cc. of strong H_2SO_4 were dealt with as though a carbon determination were being made. The increase in the absorption-bulbs was 5·5 milligrammes, equivalent on the experiments to a mean + error of 0·044 % C. As to whether this error was really due to carbonaceous matter in the re-agents, or to

the faintly visible vapour of difficultly condensed SO_3, or to both, the author is not sure; however, the corrected results of the estimations made by this process are set forth in the subjoined table:—

No. of Experiment.	Weight of Steel taken.	Weight of CO_2 obtained.	% Carbon.
1	3·00	0·0544	0·495
2	3·25	0·0536	0·446
3	3·50	0·0610	0·475
4	3·75	0·0637	0·463
5	4·00	0·0668	0·455
Mean	3·50	0·0598	0·469
Greatest difference, 0·049 %.			

But one more process now remains to be dealt with, namely, the dry combustion of the residue obtained by treating the steel with cupric chloride; this after some modifications was the method finally adopted by the author, and he has no hesitation in stating, that if conscientiously carried out, it will be found to be the most accurate and convenient process.

Before describing the manipulative details of the method, it will be well to complete the tabular comparisons of the various processes. Five estimations by that last named gave the following results:—

No. of Experiment.	Weight of Steel taken.	Weight of CO_2 obtained.	% Carbon.
1	4·00	0·0735	0·501
2	3·50	0·0626	0·488
3	3·00	0·0560	0·509
4	4·00	0·0715	0·487
5	4·00	0·0725	0·494
Mean	3·70	0·0672	0·496
Greatest difference, 0·022 %.			

The following table gives comparatively the mean results obtained from the five estimations made by each method. It should be understood, that before these results were recorded many preliminary experiments were made in each process to find out the most favourable conditions for the analysis.

Method of Liberation.	Method of Combustion.	Mean % Carbon.	Greatest difference between results Carbon %.
Galvanic ...	Dry	0·459	0·042
Chlorine ...	Dry	0·470	0·073
Cupric chloride	Wet	0·469	0·049
Cupric chloride	Dry	0·496	0·022

If the mean result of the last method, namely, 0·496 %, be taken to represent the true carbon, the greatest difference 0·022 % indicates a $\pm$ error of 0·011 %, and if the process be carried out with every care by a practised manipulator, this amount may be regarded as the experimental error to which the process is liable, being constant within reasonable limits almost independently of the mass of carbon present. This is proved by the following tables of results obtained on two steels, one considerably higher and the other much lower in carbon than the standard steel. By colour comparison with the latter, two more 14-in. ingots were selected, and bars were obtained from them in the same manner as already described for the 0·496 % steel.

The steel on which the experiments detailed in the first table (p. 28) were made registered by the colour test 0·27 % C. The second steel, the combustions upon which are recorded in the second table (p. 28), showed by colour 0·80 % C.

Mr. A. A. Blair, in his work on the *Chemical Analysis of Iron*, referring to the ammonio-cupric chloride and dry combustion process, states that "duplicate results should

rarely vary more than 0·005 of a % of carbon." In other words, working on 3 grammes of steel, a ± error of 0·000075 gramme of carbon. Odd pairs of results may

TABLE I.

No.	Weight of Steel.	Weight of CO_2.	% Carbon.
1	4·75	0·0430	0·247
2	4·50	0·0387	0·235
3	4·50	0·0402	0·244
4	4·25	0·0389	0·250
5	4·00	0·0372	0·253
Mean	4·40	0·0396	0·246
Greatest difference, 0·018 %.			

TABLE II.

No.	Weight of Steel.	Weight of CO_2.	% Carbon.
1	3·00	0·0852	0·775
2	3·50	0·1010	0·788
3	3·25	0·0946	0·793
4	3·75	0·1088	0·791
[1]5	4·00	0·1126	0·768
Mean	3·50	0·1004	0·783
Greatest difference, 0·025 %.			

[1] A little carbon was lost during filtration.

by chance agree thus closely, but a series of combustions from which alone the true experimental error can be determined, shows, as already indicated, an unavoidable difference equal to four times the percentage given by Mr. Blair.

Liberation of Total Carbon by Cupric Chloride and Dry Combustion of the Residue.

(Time occupied, about 1½ working days.[1])

Preparation of Re-agents.

No. 1 *Solution.*—Weigh out into a 60-oz. beaker, marked for 1 litre, 250 grammes of pure cupric chloride, dissolve in hot water, and make up to 1000 cc.; bring the solution to boiling, and add, drop by drop, a strong solution of caustic potash till the liquid is milky with a permanent pale-blue precipitate of cupric hydrate. Boil up well, say for 15 minutes, then allow to stand for a day or two, till the hydrate and often a yellow basic precipitate have settled. (The object of thus neutralizing with potash is to remove from the copper salt any free acid present which might liberate a small portion of the carbon in the steel in the form of gaseous hydrocarbons.[2]) Filter off the clear solution into a perfectly clean stoppered Winchester quart, rub the filter-paper well before using to detach any loose fibres and so avoid getting them into the solution. Now, as all through the analysis, rigorous precautions must be taken to prevent the accidental introduction of extraneous carbon into the estimation.

[1] The "time occupied" given with each process means the time over which the operation extends, and not that the analyst is wholly engaged for that period upon the estimation. As a matter of fact, an expert chemist with ample appliances can, in the case of certain steels, make two complete ordinary analyses in a working day of seven hours.

[2] The B. A. Committee regard such evolution as apocryphal when using ammonio-cupric chloride, but the author has observed a distinct evolution of gas bubbles with acid $CuCl_2$ solution.

No. 2 Solution.—Dissolve 600 grammes of pure cupric chloride and 300 grammes of clean common salt ($NaCl$) in boiling water. Make up the solution to 1800 cc., and then add 200 cc. of fuming HCl solution, mix thoroughly and filter, etc., as described for No. 1 solution.

Asbestos.—Fine, silky Italian asbestos must be carefully picked out into thin fibres: these are then worked up into a woolly mass, are strongly ignited in a muffle furnace, allowed to cool under cover, and are then preserved in a well-stoppered, wide-mouthed bottle.

Cupric oxide.—The purest form of this re-agent is made by cutting up into pieces about $\frac{1}{8}$th in. square, electrotype copper foil. The fragments of copper are then placed in an old porcelain dish, and are heated for several hours in the muffle till converted into oxide. This preparation the author prefers to the granulated copper oxide of the shops, which sometimes gives off even after prolonged ignition gases capable of absorption by caustic potash.

Potash pumice.—For the preparation of this re-agent a considerable quantity of pumice stone is coarsely powdered. The fine powder is then removed through a copper sieve about 7 in. in diameter, with a rim 1 in. deep, and perforated with holes $\frac{3}{32}$ of an inch in diameter. The coarser residue is treated in a similar sieve with holes $\frac{1}{8}$ in. in diameter, the fragments passing through being used for the preparation of the re-agent. The grains are placed in a porcelain dish, and potash solution is added till the pumice is saturated with it. The mass is then gently heated and stirred with a glass rod until quite dry. Any clotted masses are then carefully broken up into their constituent grains by means of the rod, and whilst still warm the re-agent is placed for preservation in a well-stoppered bottle.

Calcium chloride.—Ordinary chloride of calcium is heated, at first cautiously, in a porcelain dish till it ceases to give off water, and is converted into a dry, spongy mass. The original salt has lost two-thirds of its combined water, thus—

$$(CaCl_2, 6\,H_2O) = (CaCl_2, 2\,H_2O) + 4\,H_2O$$

The mass is broken up and sieved exactly as described for the pumice, only this exceedingly hydroscopic substance must be kept as hot as possible during the sieving operation, and the granules when obtained should receive a good final heating before being bottled. They must also be hot when introduced into the absorption-tube described later on.

Caustic potash solution.—Make when required by dissolving 25 grammes of stick potash in 50 cc. of distilled water.

Mixture of chromic and sulphuric acids.—To 100 cc. of water contained in a thin beaker add 100 cc. of strong sulphuric acid. When cold, dissolve in the mixture as much chromic acid as it will take up. Preserve for use in a stoppered bottle.

Oxygen.—This is best prepared by strongly heating in a hard glass flask pure, *dry*, powdered chlorate of potash. As soon as the fused mass begins to boil the heat must be regulated so that the evolution of oxygen is not too violent. The gas is collected in the glass gas-holder (A Fig. 7) after passing through a washing cylinder containing a strong solution of caustic soda or potash.

The Process.

Liberation of the carbon.—Weigh out from 3 to 5 grammes of the steel drillings into a 20-oz. beaker,

provided with a glass rod crusher and a concave cover. Add 25 cc. of No. 1 solution for each gramme of steel taken; allow to stand for at least four hours, occasionally well stirring and crushing the precipitated copper until no gritty feeling is any longer perceptible. Now add 50 cc. of No. 2 solution for each gramme of steel present, when the dirty-looking yellow scum of basic iron and copper salts will be dissolved. The beaker and its contents are now heated to about 60° C., and the liquid is frequently stirred till all the precipitated copper is dissolved, and nothing but carbonaceous flocks remain. The beaker is then put aside for at least an hour to allow the residue to settle. Time is thus saved, as the almost black, supernatant liquid then passes rapidly through the filter before the latter becomes clogged with carbon.

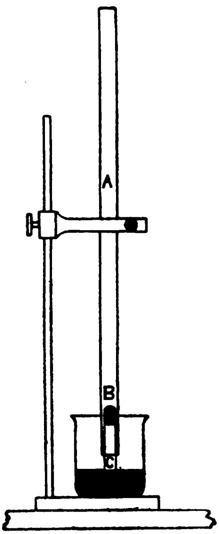


FIG. 5.

Collection of the residue.—This is effected in the filter apparatus sketched in Fig. 5. A perfectly cleaned and dried tube A about 500 mm. long by 15 *mm. inside diameter*, is supported in a wooden clamp stand; in it is packed a plug about 20 mm. long of the carefully-shredded recently-ignited silky asbestos fibres B. *This plug must be very carefully fitted.* It should be loose enough to allow the filtrate to pass through at a fairly rapid rate, but sufficiently compact to retain every particle of carbon. It is shaped and placed in position by means of a long, flat-headed glass rod and the tube C, which is 250 mm. long and 12 mm. *outside* diameter, and supports

the plug in position in the larger tube. The latter is filled up (using the stirring-rod as a guide) with the dark liquid, and as much as possible should be got through before throwing any carbon on the plug. Every particle of carbon is then carefully washed into the tube, which during the intervals of filtration should be kept covered with a little porcelain crucible lid. The beaker also should never be left uncovered. The residue is well washed with hot dilute HCl solution, and then thoroughly with distilled water till quite free from acid. This may be tested by means of dilute solution of nitrate of silver. The washings from the tube should produce no opalescence in the silver solution.

In the foregoing operation, when the dark cuprous solution has all passed through, it will be readily seen whether the packing of the asbestos has been efficient. If dark channels of carbon reach the bottom of the plug, start the estimation afresh; if, however, all is satisfactory, proceed as follows:—

Drying the residue.—Into a 3-in. porcelain dish place a roughly-made pad of ignited asbestos, about 40 mm. in diameter and 2 mm. thick. Then on to this, by means of the long, flat-headed glass rod, carefully slide the plug out of the filtration-tube, carbon side down: if this is skilfully done, not a particle of carbon will adhere to the edge of the tube. Should, however, any remain, it is removed with a small piece of ignited asbestos, the latter being placed, of course, on the pad. The dish and its contents are put into an air-bath, and maintained at a temperature of about 100° C. till the plug is quite dry.

Packing the combustion-tube.—The glass tube in which the combustion is made must be of carefully selected refractory but not brittle glass. It will only serve safely for

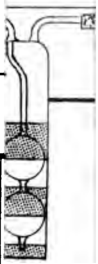
one estimation.[1] Its length should be about 700 mm.,[2] and its inside diameter *must be* 20 *mm.*, in order to allow the carbon plug to be easily inserted. The sharp edges of the tube should be removed with a file, so that they do not cut the corks. The arrangement inside the tube is shown in Fig. 6: B is a closely-packed column of fragments of recently-ignited cupric oxide (*CuO*). It is secured in position by the ignited asbestos plugs A and C. In these channels are made for the passage of the gases in the position shown in the sketch by means of a clean, stout, pointed copper wire. D is the carbon-plug, E the pad, packed and channeled as shown.

Fig. 6.

Combustion of the residue.—The tube is placed in a sufficiently long (20 tap) Hoffman or other combustion furnace, so that the pad E is at least three burners within the furnace. Into the tube are now firmly inserted the india-rubber corks, by means of which it is attached to the apparatus sketched in Fig. 7: A is a glass gas-holder containing pure oxygen (the stoppers and taps of this vessel should all be well greased); B is a bulb charged with strong caustic potash solution; C is a tube filled with potash pumice; D is the furnace and tube (the end of the latter at which the

[1] The author, after a careful comparison of the advantages and disadvantages attending the use of porcelain and glass tubes for combustions, has decided in favour of the latter.

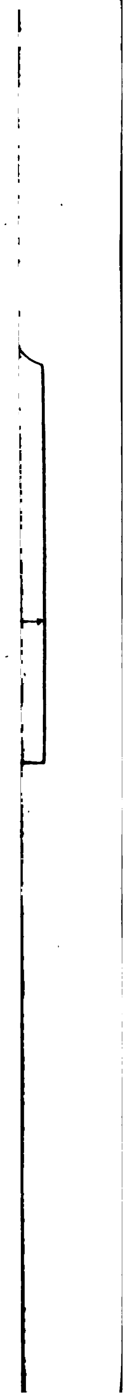
[2] A shorter tube involves the risk of scorched corks.



G

carbon plug is placed is connected with the tube C); E is a bulb charged with the mixture of chromic and sulphuric acids and water; F is a bulb containing concentrated sulphuric acid; G is a bulb charged with strong potash solution; H is a tube packed one-third (next the furnace) with potash pumice and two-thirds with dry chloride of calcium; I is a valve, the bend containing a little strong sulphuric acid to prevent the possible absorption of moisture by the tube H from the aspirator J. The parts of this apparatus must be tightly coupled up with *sound* thick-walled rubber tubing. The tightness of the apparatus should be tested by coupling everything up, closing the gas-holder, and opening the aspirator tap, when the passage of the air through the bulbs soon ceases if the whole arrangement is air-tight. Nip the tube attaching I to the aspirator, and remove and replace the bung of the latter to restore the equilibrium. All being ready, the gas-holder is detached from C, and a litre of air is gently aspirated through the system to remove all CO_2. The aspirator tap is shut and the gas-holder is re-attached to C, the tap opened, and a steady stream of gas is passed through the apparatus till the pressure is equalized. The absorption-tubes G and H are now detached, their open ends as well as those of F and I being stoppered for the time being with little pieces of india-rubber tubing, closed at one end with glass rod. The absorption-tube H is provided with a horse-hair loop, which serves to suspend it on the hook of the balance-pan. The tubes are placed for five minutes in the balance-case, and are then very carefully weighed without their stoppers, having been previously wiped with a clean old linen handkerchief. Having been re-attached to the apparatus, the combustion is proceeded with as follows: slightly open the aspirator tap and that

of the gas-holder, so as to pass through the bulbs a gentle bubble by bubble current of oxygen, which must be maintained throughout the operation. The first burner under the copper oxide (next E) is very cautiously lighted by means of a taper, the gas being quickly and repeatedly turned in and out till the tube is warm enough to have evaporated the condensed moisture first formed from the vicinity of the burner. *If this precaution is not faithfully carried out, the probability is that the tube will crack.* Next, one by one, with the same precaution, light alternate burners under the copper-oxide till the whole column is being heated; then place the fire-clay covers over this portion of the tube. As soon as the oxide is red-hot, quietly one by one light the jets to the end of the furnace next C. The carbon flashes off and burns readily, but the heat should be continued after having placed on the remainder of the fire-clay covers till the asbestos plug is thoroughly red-hot. The portion of the tube containing the copper oxide must be watched, and if it shows any signs of sagging out, the temperature at that point must be moderated by turning out a tap or two. As soon as the combustion is finished the gas-holder tap is shut, the tube nipped and detached, and the air is very gradually admitted till the pull of the aspirator is normal. At least a litre of air is then aspirated, the absorption-tubes are detached with the precaution already given, are stoppered, and after remaining five minutes in the balance-case are again wiped and re-weighed. The increase registers the weight of CO_2, which contains 27·27 % of carbon. (If the precautions advised during the various detachments of the parts of the apparatus are not observed, the violent passage of gas through the liquid re-agents may splash them from one tube to the other, a disaster necessitating a long delay for re-filling.)



Details of apparatus.—A dimensioned sketch (Fig. 8) of one of the wooden stands used to support the above apparatus may be useful. It will be noted, that the only movable corks employed are those in the combustion-tube. The dry absorption-tubes are of special design

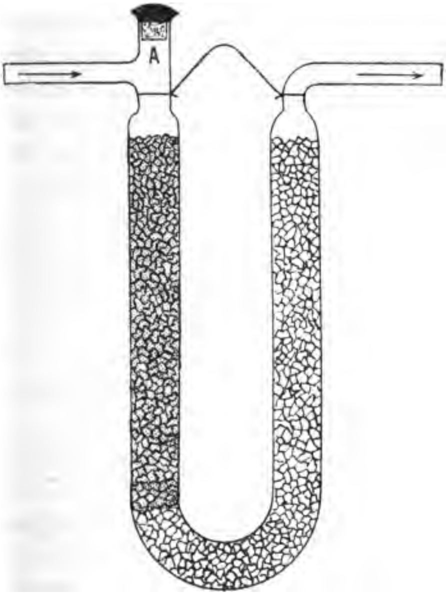


FIG. 9.

(Fig. 9): they are filled through a little funnel at the neck A, through which the pumice or chloride of calcium granules are shaken. When filled, the neck is firmly corked and hermetically closed by sealing-wax, the latter being carefully heated over a small Bunsen flame till smooth and rounded. Every chemist who has been engaged in organic analysis will have had painful experience of the fragile nature of Geissler's bulbs. The author has therefore

designed a potash bulb combining efficiency, strength, and simplicity. It is sketched in Fig. 10. The space between the cylinder and the two inner bulbs should not exceed 0·20 mm. When this dimension is correct, pressure through the inlet tube splits up the liquid into three layers, so that gas passing through these bulbs first comes into contact with the film of the re-agent on the inside of the bulbs; it then passes through the lower layer of absorbent, is next placed between the lower and middle layers of the liquid, then passes between the moist surfaces of the first bulb and the cylinder in a layer only 0·2 mm. thick; again bubbles through the absorbent, and passes into the space between the second and third layers of liquid; once more passes between the bulb and cylinder, and finally bubbles through the upper layer of absorbent. The bulbs present comparatively little outer surface to the condensation of moisture, and every part of them is readily wiped before weighing.

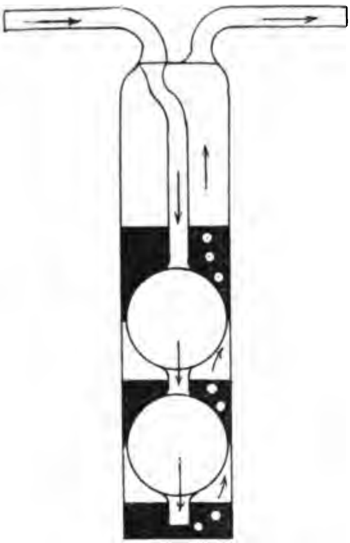


FIG. 10.

Theory of the Combustion Process.

The action of No. 1 solution removes the iron from the carbon with which it is combined or mixed as the case may

be, and leaves the latter in flocks, mixed with metallic copper, thus respectively—

$$Fe_3C + 3\ CuCl_2 = 3\ FeCl_2 + 3\ Cu + C$$
$$Fe + CuCl_2 = FeCl_2 + Cu$$

In the first reaction carbide of iron and cupric chloride yield ferrous chloride, copper, and carbon. In the second reaction the iron is merely removed as ferrous chloride, leaving admixed graphite and copper.

The ferrous chloride in solution oxidizes from the air, and basic ferric chloride is precipitated in yellowish flakes. From the action of the excess of cupric chloride present upon the precipitated copper, dirty-white cuprous chloride is precipitated, this salt being insoluble in a neutral solution. These precipitates, however, are readily dissolved by the free HCl in the No. 2 solution, the latter also acting upon the copper thus—

$$CuCl_2 + Cu = 2\ CuCl$$

Cupric chloride and copper yield cuprous chloride soluble in HCl. The presence of the sodium chloride assists the solution of the copper by forming a double chloride, $CuNaCl_2$. The carbonaceous residue contains combined water, often some silica and phosphide of iron, and particularly sulphide of copper. The latter in steel high in sulphur and low in carbon may, by the production of SO_2 during the combustion, give rise to serious error, hence the mixed chromic and sulphuric acids bulb E, which oxidizes the gaseous SO_2 to sulphuric acid,[1] in addition to con-

[1] The author made the following experiments on a basic steel or rather iron ingot, containing under 0·1 % of carbon and 0·09 % of sulphur, in consequence of the carbon by combustion being considerably higher than that obtained by the colour test. A residue from 3 grammes of steel was collected upon a paper filter, and after thorough washing, was dried at 100°. The dried mass was removed

densing the bulk of the water given off by the residue. The latter may also contain tungsten and chromium, so that the student need not be alarmed at a pink (Fe_2O_3), yellow (WO_3), greenish (Cr_2O_3), or dark (CuO) residue remaining on the plug after the strong ignition in oxygen.

The tubes B and C serve to thoroughly purify the oxygen from any gases capable of being absorbed by potash.

The column of oxide of copper ensures the conversion of any small quantity of CO (which is insoluble in potash) that might be produced during the burning of the carbon, thus—

$$CO + CuO = Cu + CO_2$$

Carbonic oxide and cupric oxide yield copper and carbonic anhydride. It also seems to prevent any traces of chlorine present in the residue getting forward to the potash bulbs by converting it into $CuCl$; the latter may be occasionally seen as a faint brown sublimate on the portion of the tube just in front of the oxide. The sulphuric acid bulb F serves to remove the last traces of moisture from the gases before passing to the potash bulb G; the latter absorbs the CO_2 thus—

$$CO_2 + 2\ KHO = K_2CO_3 + H_2O$$

Carbonic anhydride and potassic hydrate yield potassic

---

from the paper, transferred to a beaker, and boiled with strong nitric acid. The solution was evaporated to dryness, and the dried mass was extracted with water containing a few drops of HCl. The liquid was filtered off, and a few drops of a 10 % $BaCl_2$ solution was added: a precipitate of $BaSO_4$ was at once obtained.

Another residue was prepared and burnt off exactly as for a combustion, the gases, however, being passed after leaving the combustion-tube into a Geissler apparatus containing an acidified solution of potassium permanganate. The first bulb was totally and the second partially decolorized by the evolved SO_2.

carbonate and water. The formation of the crystals of carbonate of potash may often be watched inside the bulbs. The potash pumice in the first limb of the tube H absorbs most of the moisture taken up by the gases when passing through the potash solution: if the tube were totally filled with calcic chloride the latter would soon liquefy, cake in the upper part of the limb, and thus prevent the passage of the gases. The chloride of calcium filling the remainder of the tube effectually prevents any moisture being carried away. Mr. Blair, on page 113 of his book on *Iron Analysis,* makes a statement to the effect, that moist gas passing through a small quantity of sulphuric acid contained in the bend of a bulbed U tube, is drier on leaving it than when passed through a U tube entirely packed with dry, granulated chloride of calcium. He therefore introduces into his moist combustion apparatus a plug of damp cotton-wool, in order that the gases may issue from his absorption-tube with the same degree of humidity they possessed when entering. With reference to the above statement and procedure, the author may mention that he has frequently checked the absorptive power of such a chloride of calcium tube during a combustion by passing the gases from it through a weighed Geissler bulb containing strong sulphuric acid. No practical increase in the latter was ever obtained—in fact, with a column of spongy chloride of calcium only 2 in. long by ½ in. diameter, the mean of three experiments registered the moisture reaching the sulphuric acid as 0·0008 gramme, equivalent to a loss on three grammes of steel of 0·007 % of carbon.

With reference to the number of combustions capable of being carried out with the foregoing arrangement, the tubes B C F and H should serve, with care, for fifty estimations,

but the bulbs E G and the valve I should be re-charged for every ten estimations. When not in use every portion of the apparatus should be tightly stoppered, and the absorption-tubes are perhaps best preserved in the balance-case.[1] The following model of the record of a carbon by combustion may be useful to the student:—

July 13, 1888.

Carbon by combustion on drillings marked SD.
Weight of steel taken 3 grammes.

Weights of absorption-tubes before combustion:

KHo bulb, 34·4410
$CaCl_2$ tube, 59·1505
93·5915

Weights of absorption-tubes after combustion:

KHo bulb, 34·4670
$CaCl_2$ tube, 59·1844
93·6514
93·5915
·0599 gramme CO_2
27·27
4193
1198
4193
1198
3)1·633473
0·544 % Carbon.

As the author's experience has taught him that students who have been through a course of chemical arithmetic, and are supposed to know all about it, are often, as a

[1] The student should grasp the fact, that the weight of invisible condensed vapour, always under ordinary circumstances present upon the surfaces of glass, porcelain, and platinum apparatus, varies palpably with comparatively small differences in the temperature of the vessels, so that the absorption-tubes in each set of weighings should have as nearly as possible coincident temperatures. Hence the advisability of leaving them in the balance-case for some minutes before each weighing.

matter of fact, all at sea when a practical application of their knowledge is required, here, once and for all, the principle involved in the calculation of the percentage of the element in any weighed precipitate, etc. from a known weight of the original substance, will be fully set out. The foregoing is a short method for practical calculations, based upon and giving exactly the same result as the long method, which is as follows :—

If 100 grammes of CO_2 contain 27·27 grammes of carbon
0·0599 „ „ „ x „ „
As 100 : 0·0599 : : 27·27 : x

$$x = \frac{0{\cdot}0599 \times 27{\cdot}27}{100} = 0{\cdot}0163 \text{ gramme C.}$$

If 3 grammes of steel contain 0·0163 grammes of C.
100 „ „ „ x „ „
As 3 : 100 : : 0·0163 : x

$$x = \frac{0{\cdot}0163 \times 100}{3} = 0{\cdot}544\ \%\ \text{C. as before.}$$

Calculation of Percentage Composition of CO_2

$$C = 12 \times 1 = 12$$
$$O_2 = 16 \times 2 = 32$$
$$44$$

44 parts by weight of CO_2 contain 12 parts by weight of Carbon.
100 „ „ „ x „ „ „
As 44 : 100 : : 12 : x

$$x = \frac{100 \times 12}{44} = 27{\cdot}27\ \%$$

Estimation of Combined Carbon by the Colour Test (Eggertz).

(Time occupied, about ¾ hour.)

The most used and abused process in the whole range of iron and steel analysis.[1]

To avoid errors in making the colour test, the student should bear in mind the following facts:—

1. That the colour varies with the form (excluding graphite) in which the carbon exists in the steel: annealed steel gives a somewhat different tint from that obtained from the same steel in a normal state, although in both cases the carbon exists in combination with the iron.

[1] It is usual in text-books to state that the process consists in estimating the depth of colour produced in a dilute nitric acid solution of the steel, the intensity of the brown colour being proportional to the combined carbon present. This preamble is followed by directions to prepare by combustion a standard steel containing about 1 °/ₒ carbon to be used for the comparisons. It cannot be too strongly stated, that the colour is *not* proportional to the carbon present, except under certain special conditions, and even then within a limited range. No competent steel analyst would ever think of using a 1 °/ₒ standard to estimate the carbon in a mild steel. The authors of almost every work on iron and steel analysis which has been published during the last fifteen or twenty years have been so imbued with the proportional colour fallacy, that they figure with monotonous regularity a stand containing a long vista of hermetically sealed "proportional colour" tubes, charged with either very weak coffee or with so-called permanent colour solutions of inorganic metallic salts. The articles describing this delusion usually end up with the complacent assurance, that by its means combined carbon "may be readily determined within 0·01 °/ₒ." A friend of the author's has for some time been watching with interest the molecular changes taking place in the tubes of a rack of "permanent colour standards" in which, in a moment of weakness, he invested two guineas. At present the 0·1 °/ₒ standard is darker than the 0·3 °/ₒ.

Hardened steel, in which comparatively little carbide of iron is present, yields a much lighter colour than that obtained from the normal steel.

2. With, as far as we know, coincident forms of carbon, the colour of the solution obtained from a hard steel is found to be deeper than that obtained from a mild steel, when volumes of the liquids containing the colouring matter have been adjusted in accordance with the percentages of carbon obtained by combustion, that is to say, a 1 % steel when compared with a 0·25 % standard would register, after a fashion, considerably over 1 %. Coincident tints, however, would never be obtained. (See paragraph 4.)

3. Normal, crucible, open-hearth, and Bessemer steels of like carbon do not give exactly the same shade of colour.

4. Colours may be obtained of equal depths but varying tints.

5. The colouring matter is sensitive to daylight, being distinctly paler when exposed for a few hours.

6. The colour is not due to dissolved carbon in the elementary condition, but to an organic compound consisting of carbon, hydrogen, and oxygen. Variations in the composition, and consequently colour, of this compound are probable.

7. Over-heated steel sometimes gives to nitric acid a peculiar deep, blood-red tint. The cause of this phenomenon is obscure, but well worth investigation. Mr. E. C. Ibbotson, one of the senior students of the Sheffield Technical School, brought under the notice of the author a case in which an over-heated open-hearth ingot, containing 0·2 % of carbon, gave a colour which as nearly as could be estimated recorded the carbon as over 2 %. In another case a small steel shot, accidentally somewhat over-heated in "letting down" to drill for analysis, contained in the

centre 0·85 % of carbon, whilst the outside registered about 1·15 %. These cases are remarkable, because with a burnt steel a low carbon result is usually expected.

8. Colour tests on mild steels are more reliable than those registered by hard steels.

From the foregoing paragraphs may be deduced the ideal conditions under which this process should be employed.

(*a*) The standard and the steel to be tested should have been made by the same process.

(*b*) The standard and steel should be in the same physical condition as far as this can be secured by mechanical means.

(*c*) The standard should not differ greatly in its percentage of carbon from that present in the steel under analysis.[1]

(*d*) The solutions of the steels and standards should be made at the same time and under identical conditions, and the comparisons should be made without delay.

(*e*) Above all, the standard should be above suspicion, its carbon contents having been settled as the mean of several concordant combustions made on different weights of steel from a homogeneous bar.[2]

When all these conditions are observed, a more accurate analytical process than the colour test cannot be desired, but the author is too well aware that very often an observance of all the precautions quoted in the ideal case

[1] The standards employed at the Sheffield Technical School consist of a set of seven steel bars, ranging in carbon from 0·09 to 1·60 %.

[2] Since writing the above, the author and A. A. Read have shown (*Journal Chemical Society*, Aug. 1894) the possible existence of a subcarbide of iron, and the certain existence of double carbides of iron and manganese. The last-named seem to give a lighter colour than carbide of iron *per se*. (See memoir above quoted.)

is not possible; however, most of the conditions can always be secured, and if even these are followed, the colour test, though not accurate in every instance, is nevertheless of the greatest practical value, on account of the rapidity with which the results can be obtained.

The Process.

Sampling the steel.—This is a matter requiring a little consideration, or misleading reports may be handed in. In steel bars, and particularly billets, surface drillings should be avoided, as they are lower in carbon than the main portion of the steel. In one case in the author's experience, several tons of 3-in. billets of specified carbon "seventy" = 0·7 % were rejected on the ground that several independent analysts had returned results showing them to vary in carbon from 0·25 to 0·35 %. On investigating the matter, it was found that the drillings sent for analysis had been skimmed with a very wide angle drill from the surface of the billets. Deeper drillings from the same places sent to one of the analysts were reported by him to contain by colour test 0·69 % carbon.

When the heat is considered to which it is necessary to raise a 16-in. ingot before rolling into billets, it is not surprising that some of the surface carbon should be oxidized.

In the case of cemented steel bar (blister steel) the colour test is of dubious accuracy, firstly, because the colour yielded by this material is difficult to match with an ordinary standard; and secondly, because it is not easy to get an average sample even from a single bar.

During the process of cementation the carbonization

proceeds from the outside of the bar. This, therefore, is much richer in carbon than the middle, at all events, in the case of mild shearing bars showing "sap," and containing about $\frac{3}{4}$ % of carbon. The best plan (after cleaning both sides from rust and scale) is to drill right through the bar, and thoroughly mix the whole of the drillings; even then it is advisable to do several estimations, and take the mean of the results.

Steel which has been hardened and tempered should always be thoroughly "let down" by cautiously heating the material to a fair red, and then allowing it to cool in air before sampling. All drillings should be taken with dry tools, quite free from oil, etc. *Filings are worthless*, and particles of scale, sand, etc. should be carefully avoided. In the case of very thin sections of steel, incapable of being drilled, the sample should be filed bright on both sides, and be then sheared into small pieces suitable for weighing out for analysis.

Weighing out.—In open hearth and Bessemer steel works the analyst is usually aware of the approximate carbon in the steels to be tested, from the fact that the heats or blows have been made for special purposes, such as dead-mild, carbon, 0·1 %, Bessemer rails, 0·45 %, open-hearth wagon springs, 0·65 %, etc., so that each day's dead-mild heats are dissolved up with and tested by the dead-mild standard, spring heats with the spring standard, and so on. In crucible steel works the fractures of the ingots convey to an experienced eye a fairly accurate idea of the percentage of carbon present. In cases where the carbon is absolutely unknown a preliminary trial must be made, in order to find out roughly what carbon is present, so as to compare it with the nearest standard. The following table shows the weights required of various percentages

of carbon, the volume of dilute nitric acid required in each case, and the approximate percentage of carbon in suitable standards.

% C. in Steel.	% C. in Standard (approximately).	Weight of Steel, grammes.	Size of test tube, inches.	Vol. of Acid, cc.
1·3 to 1·7	1·50	0·05	$6 \times \frac{1}{2}$	3
1·1 „ 1·3	1·20	0·05	„	3
0·8 „ 1·1	0·90	0·10	„	4
0·4 „ 0·8	0·60	0·10	„	3
0·2 „ 0·4	0·30	0·10	„	2
0·1 „ 0·2	0·15	0·30	6×1	6

The test tubes used should be of thin glass, and preferably of equal bore; they must be *scrupulously clean*, and *quite dry* inside. A slip of gummed paper should be attached to each, and upon this should be legibly written the carbon contents of the standard, or the distinguishing mark of the steel to be tested, as the case may be. The tubes are then conveyed to the balance in a rack. Having carefully weighed out the steels, transfer the drillings by tapping and, if necessary, by brushing without loss to their proper tube.

Dissolving the sample.—To each tube the requisite volume of chemically pure (chlorine free) nitric acid of specific gravity 1·20[1] is added from a 50 cc. burette. The tubes are then left in the rack for a few minutes till the first violent evolution of nitrous fumes has ceased. The brown organic flocks containing the carbon will then be noted floating about in the already coloured acid. The tubes are next placed on the hot plate in a bath of just boiling water, and are occasionally shaken till bubbles of

[1] Best made by the hydrometer. It may, however, be approximately obtained by mixing 250 cc. distilled water with 175 cc. of nitric acid of specific gravity 1·43.

gas are no longer given off, and the solutions are clear. This will be in from 15 to 30 minutes—the time varying with the quantity of brown flocks to be dissolved. It will be found that when the tubes are placed in a slanting position, some of the solution of ferric nitrate is liable to dry on the sides; also, that when they touch the bottom of the bath, bumping sometimes occurs. To remedy this, the author designed the carbon bath sketched in Fig. 11. The specially made glass beaker has no radiused sides; it measures 5 in. in diameter by 5 in. deep. The glazed china cover is perforated with holes, either $1\frac{1}{8}$ in. or $\frac{5}{8}$ in. in diameter, to admit the two sizes of test tubes employed. The tubes are supported on the cover by means of nicely-fitting india-rubber gauge glass rings, slipped on to the tubes to such a height that their bottoms are about one inch from the beaker. When the solution is complete, the tubes and their contents must be well cooled in a vessel of cold water before testing, because the liquids are much darker whilst hot than when cold.

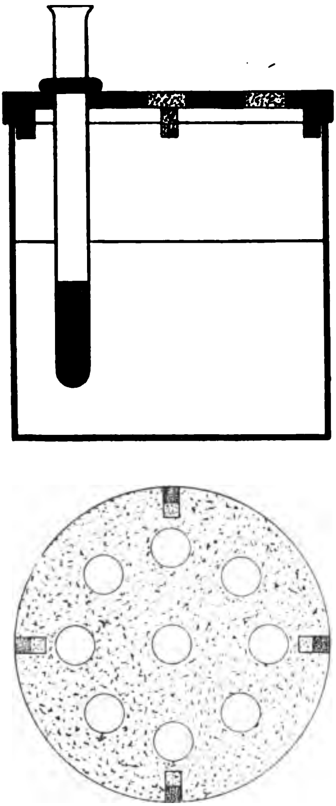


Fig. 11.

Comparing the colours.—The pairs of graduated tubes used for this purpose are conveniently of two sizes. Each pair must be of equal bore and thickness of glass, and the latter should be untinged with colour. The tubes must always be thoroughly washed out before using. The first pair should be 12 cc. graduated in tenths, and have an inside diameter of about 10 mm. They are used for all steels containing 0·2 % and upwards of carbon. The second pair, used only for steels containing between 0·1 and 0·2 % of carbon, should be of 20 cc. capacity, graduated in half cc. One of each pair of tubes should be marked S with a diamond: into this cautiously pour the solution of the standard steel, rinse out the dissolving-tube with a small quantity of distilled water, of course pouring the washings into the comparison-tube. The liquid in the latter is now very carefully diluted to the mark by means of a fine jet of distilled water: be careful not to overshoot the point, remembering that the drainings from the side of the tube will usually measure nearly $\frac{1}{10}$ of a cc. Close the mouth of the tube with the finger—*which should be clean*—and invert the liquid two or three times till of even colour throughout. Treat the steel to be tested in a similar manner, not of course filling to the mark, but gradually diluting and mixing the solution till the tints in the two tubes as nearly as possible match. The percentage is then read off. Probably the best and certainly the simplest background against which to compare the colours is a piece of clean filter-paper saturated with water, and stuck upon a pane of glass in a window having a north light; in any case, sunlight must be avoided. In determining the final point change sides with the tubes, because it will usually be found that an apparent match of tints is disturbed by this alteration in

relative position. When a point is reached at which the steel being tested looks a shade light on one side and a shade dark on the other side of the standard, the true reading has been obtained. The following table will indicate to the student the manner in which the standards are diluted, and the volumes of liquid registered by the unknown steels are read off as percentages. The carbons in the table are given in round numbers. In actual practice figures in the second decimal place will probably be involved, when of course the dilution of the standard is made to correspond thus, a 0·78 % standard must be diluted to 7·8 cc.

C. % in Standard.	Dilute Standard to cc.	To convert cc. registered by Steel into Carbon %.
1·50	7·50	Divide them by 5
1·20	6·00	" " 5
0·90	9·00	" " 10
0·60	6·00	" " 10
0·30	3·00	" " 10
0·15	15·00	" " 100

Steels leaving a Residue insoluble in Nitric Acid.

High carbon steels occasionally leave a black residue of graphite, high tungsten steels deposit yellow tungstic acid, and wrought iron, puddled, and blister steels sometimes leave a small dark powdery precipitate of slag, etc.[1] All these solids require filtering off before making the comparisons. A plain funnel one inch in diameter, containing a minute circular filter-paper,[2] is supported over

[1] This fact may serve to distinguish wrought iron from dead-mild steel.

[2] A penny serves very well to cut this out to.

the graduated tube in such a manner that the stem of the funnel reaches about half an inch down the tube. The solution is then passed through the filter, the latter, the dissolving tube and the residue, being of course washed colour-free with a fine jet of distilled water. The clear liquid is then compared as already described.

Steels for which the Colour Test is not available.

These comprise steels containing large percentages of elements yielding coloured solutions with nitric acid: such are chromium, copper, and nickel, particularly the first-named metal. When only moderate percentages of nickel or copper are present, fairly accurate colour results may be obtained, and the same remark applies to very small percentages of chromium. In certain special steels, where the percentage of the colouring element is practically constant, a standard containing the same amount of that element may be prepared. In some instances the author has found a modified application of the alkaline colour test devised by Mr. Stead[1] for the determination of carbon in ingot iron to be useful, inasmuch as chromium, nickel, and copper are precipitated as hydrates along with the iron by the caustic soda employed in this process, but as a rule the safest way out of the difficulty is to estimate the carbon by the combustion method.

Determination of Graphite in Steel.

Graphite occurs in steel when the latter has contained a high percentage of combined carbon, and has been under

[1] *Journal of the Iron and Steel Institute*, 1883, No. 1, page 213.

the influence of certain abnormal physical conditions. For instance, the author has found that by prolonged annealing it is possible to convert most of the carbon in a steel containing say 1·5 % of that element from the combined to the graphitic condition. Again, in rolling hard file steel, the unwelcome phenomenon of a partial separation of graphite sometimes occurs, resulting in the production of what is technically known as "black steel."

The determination of graphite is often made by dissolving the steel in hydrochloric acid, diluting the solution, collecting the insoluble residue on a paper filter, washing it with hydrochloric acid and water, and afterwards with caustic potash solution and water, to dissolve out the silica. The residue, or as much of it as is possible, is then washed from the paper into a platinum dish—the contents of the latter are evaporated to dryness—the dish and its contents are weighed, strongly ignited and again weighed, and the difference between the two weighings is taken as graphite. This method is a slovenly process, open to several objections, and the author strongly advises the student not to use it. When a determination of graphite is worth doing at all, it is worth doing accurately, especially as this occupies very little more time than the crude method just briefly described.

Determination of Graphite by Combustion.

Weigh out 5 grammes of the steel into a 20-oz. beaker, put on the cover, and add cautiously in several portions 100 cc. of dilute nitric acid, spec. gravity 1·2. Digest the solution at about 100° C. until all the iron, and the flocks containing the combined carbon, have passed into solution;

collect the residue on asbestos exactly as described on page 32, washing, however, first thoroughly with cold water, then with very dilute ammonia (1 cc. of liquid ammonia, spec. gravity 880, mixed with 99 cc. of distilled water), and finally with hot water. Dry and burn the residue, collecting and weighing the evolved CO_2 exactly as described on page 33 *et seq.*, igniting, however, *as strongly as possible*, graphite being much less combustible than the residue containing combined carbon.

Theoretical Considerations.

The author prefers to dissolve the steel in dilute nitric instead of hydrochloric acid, in order to sharply separate the combined from the free carbon. The latter acid, it is true, evolves most of the carbide carbon in the form of gaseous hydrocarbons, but in high carbon steels, in which only the determination of graphite is likely to be required, more or less combined carbon, which has escaped from or evaded combination with the hydrogen, remains with the graphite in the solid form. With the strength of acid specified, and at the temperature given, the author is of opinion that no graphite is converted into CO_2 or passes into solution. Another advantage of nitric acid is, that it retains the silicon (sometimes in the case of steel castings present in considerable quantity) in solution, whereas *HCl* liberates it as gelatinous silicic acid, which seriously impedes the rapidity of the filtration. The reason for using cold water in washing away neutral or faintly acid solutions of iron salts may be here stated once and for all. *Hot water is very liable to throw down precipitates of insoluble basic iron salts into the pores of filter-paper or*

asbestos. The dilute ammonia converts any free nitric acid in the residue or asbestos into nitrate of ammonia, thus—

$$HNO_3 + NH_3 = (NH_4)NO_3$$

Any traces of the latter salt present on burning the residue are converted into water, oxygen, and nitrogen, thus—

$$(NH_4)NO_3 = 2\,H_2O + N + O$$

If any nitric acid remains in combination with the graphite, it will during the combustion be converted into water and brown peroxide of nitrogen gas thus—

$$2\,HNO_3 = H_2O + 2\,NO_2$$

The latter will be absorbed in the sulphuric acid drying bulb, forming nitro-sulphonic acid.

The Action of Acids on Steel.

Before going on to describe the estimation of elements other than carbon, it will be well to tabulate for the student the reactions of acids upon steel. It is, however, only necessary to consider those obtained with

$$\left.\begin{array}{l}\text{Hydrochloric acid}\\ \text{Sulphuric acid}\end{array}\right\}\begin{array}{l}\text{Weak}\\ \text{oxidants.}\end{array}$$

$$\left.\begin{array}{l}\text{Nitric acid}\\ \text{Aqua regia}\end{array}\right\}\begin{array}{l}\text{Powerful}\\ \text{oxidants.}\end{array}$$

Hydrochloric Acid.

The liquid usually known in the laboratory by this name is really a saturated solution of gaseous *HCl* in water: it has a spec. gravity of about 1·2, and contains approximately about 40 % of true *HCl*. The reactions

of this strong solution on the elements of steel may be formulated thus—

Iron is converted into pale-green ferrous chloride, which remains in solution whilst the co-produced hydrogen gas escapes thus—

$$Fe + 2\,HCl = FeCl_2 + 2\,H$$

Carbon existing as carbide of iron is almost totally converted into gaseous hydrocarbons, which escape. This is due to the action on the carbon of the nascent hydrogen liberated from the acid.

Graphite remains suspended in the solution; it may, however, to some extent absorb or form weak compounds with the acid or gases present.

Silicon existing as silicide of iron is probably, at the moment of its liberation (in the nascent condition) from the iron, oxidized by the water present to gelatinous silicic acid with an evolution of hydrogen, thus—$Si + 4\,H_2O = H_4SiO_4 + 4\,H$. The silicic acid remains partly suspended and partly dissolved in the acid.

Manganese existing alloyed with the iron and carbon, liberates hydrogen from the acid, and remains in solution as manganous chloride, thus—

$$Mn + 2\,HCl = MnCl_2 + 2\,H$$

Sulphur existing as sulphide of iron is totally converted into invisible sulphuretted hydrogen gas, which escapes, thus—

$$FeS + 2\,HCl = FeCl_2 + H_2S$$

Phosphorus existing as phosphide of iron remains to a slight extent in solution as phosphate of iron $FePO_4$; most of it, however, escapes as phosphuretted hydrogen PH_3.

Arsenic existing as arsenide of iron is converted by the strong acid into volatile liquid arsenious chloride $AsCl_3$, very liable to escape as vapour.

Tungsten existing alloyed with the iron and carbon remains chiefly as a dark, insoluble residue, consisting of a mixture of the metal and its lower oxides, the latter being to some extent soluble in the acid.

Chromium existing alloyed with the iron and carbon is probably in the first instance converted into blue chromous chloride, with evolution of hydrogen, thus—$Cr + 2\,HCl = CrCl_2 + 2\,H$; the chromous salt, however, is very rapidly converted into green chromic chloride by atmospheric oxygen, thus—

$$2\,CrCl_2 + 2\,HCl + O = 2\,CrCl_3 + H_2O$$ [1]

Nickel existing alloyed with the iron and carbon evolves hydrogen from the acid, and remains in solution as pale-green nickelous chloride, thus—

$$Ni + 2\,HCl = NiCl_2 + 2\,H$$

Aluminium existing alloyed with the iron remains in solution as chloride, hydrogen being given off, thus—

$$Al + 3\,HCl = AlCl_3 + 3\,H$$

Copper existing alloyed with the iron is sometimes present in small quantities, and remains in solution as green cupric chloride, $CuCl_2$.

Titanium.—It is very dubious whether this element is ever present in commercial steel; if so, it will be converted into soluble titanic acid, thus—

$$Ti + 4\,H_2O = H_4TiO_4 + 4\,H$$

Sulphuric Acid.

The concentrated acid, sp. gravity 1·834, practically corresponds to the formula H_2SO_4. Steel is little soluble

[1] In very rich chrome steels a small insoluble residue of carbide of chromium may remain.

in the strong liquid, the sulphates formed, being insoluble in the acid, coat the metal and protect it from further action. The dilute acid used as a solvent for steel is made up of one volume of the strong acid and six volumes distilled water. The action of the dilute acid on steels is almost perfectly analogous to that of HCl, only, of course, the corresponding metallic sulphates, $FeSO_4$, $Al_2(SO_4)_3$, etc., are produced. As a rule, HCl is the most convenient to use, but when it is desired to retain the solution of iron in the ferrous condition, sulphuric acid is distinctly superior, because ferrous sulphate ($FeSO_4$) is not nearly so readily oxidized by the air to ferric sulphate ($Fe_2(SO_4)_3$) as is ferrous chloride ($FeCl_2$) to ferric chloride ($FeCl_3$).

Arsenic, however, remains as dark arsenide of iron, liable to be converted into arsenious acid $As(HO)_3$, and some of the latter may be reduced by the action of the nascent hydrogen AsH_3 being evolved.

Nitric Acid.

The strong acid, sp. gravity 1·43, contains about 68 % of true HNO_3; it has no action on steel in the cold (the metal assuming what is known as the passive condition), and even on boiling the dissolution is very slow. The acid used for a steel solvent has a specific gravity of 1·2, and contains about 34 % of true HNO_3. The attack of this dilute acid on steel is violent. The reactions taking place are as follows :—

Iron is converted into pale-green ferric nitrate $Fe(NO_3)_3$, which remains in solution, and the brown oxides of nitrogen N_2O_3 and N_2O_4 are thrown off.

Carbon has already been dealt with in the article on the colour test (see p. 44).

Graphite.—The dilute acid does not seem to form any volatile or soluble carbon compounds with this substance. It is possible, however, that the graphite absorbs or forms weak compounds with the acids and gases present.

Silicon remains in solution as silicic acid, which appears to form with the nitric acid and nitrate of iron some compound which does not decompose when heated at 250° C., and is soluble in HCl. The silica, however, separates on evaporating down the last-named solution.

Manganese remains in solution as manganous nitrate $Mn(NO_3)_2$.

Sulphur is oxidized to sulphuric acid, and remains in solution as ferric sulphate $Fe_2(SO_4)_3$.

Phosphorus is oxidized to phosphoric acid, and remains in solution as ferric phosphate $FePO_4$.

Arsenic is oxidized to arsenic acid, and remains in solution as ferric arsenate $FeAsO_4$.

Tungsten is oxidized to tungstic acid H_2WO_4, which passes into solution. In self-hardening steels, however, in which the percentage of tungsten is very high (10 %), a portion of the metal is precipitated as insoluble yellow WO_3.

Chromium, when present in small quantities, passes into solution as chromic nitrate $Cr(NO_3)_3$. When, however, it is present to any great extent, it remains in the form of insoluble metallic scales of impure chromium.

Nickel passes into solution as nickelous nitrate $Ni(NO_3)_2$.

Aluminium remains in solution as aluminic nitrate $Al(NO_3)_3$.

Copper passes into solution as cupric nitrate $Cu(NO_3)_2$.

Titanium is oxidized, and remains dissolved as titanic acid H_4TiO_4.

Nitro-hydrochloric Acid or Aqua Regia.

On mixing together strong nitric and hydrochloric acids, the two combine and form a yellowish-red fluid of great use as a powerful oxidizing agent. The liquid contains in solution two gases, namely, deep yellow nitrosyl chloride and free chlorine. The reaction may be expressed thus—

$$3\,HCl + HNO_3 = NOCl + Cl_2 + 2\,H_2O$$

For the purposes of steel analysis this re-agent should be made by mixing four volumes of concentrated hydrochloric acid solution and one volume of strong nitric acid (sp. gr. 1·43). These proportions are important in connection with a point bearing upon the estimation of silicon, which will be referred to later on (*vide infra*). When the liquid has acquired its full colour, which will be in the course of a few hours, it is ready for use. Its reactions upon the elements of steel are in some instances similar to those of nitric acid, whilst in certain cases they are the same as those obtained with HCl.

Iron is violently attacked, and passes into solution as deep yellow *ferric* chloride $FeCl_3$ (HCl alone yields *ferrous* chloride $FeCl_2$).

Combined carbon is no doubt to some extent oxidized to CO_2, but the greater portion passes into solution, and on evaporating the liquid separates out in the form of a finely-divided brownish precipitate.

Graphite is possibly to a small extent oxidized to CO_2, but the bulk of it remains as an insoluble residue. It

is probable, however, that it forms a weak compound with the acids and gases present.[1]

Silicon is oxidized to silicic acid, most of which passes into solution: it, however, entirely deposits on evaporation to dryness as insoluble SiO_2, *providing the volume of strong hydrochloric acid before specified is used for the preparation of the re-agent.* If too much nitric acid is present the whole of the silica is not rendered insoluble, some of it passing into solution again when the dry mass is taken up in HCl.

Manganese remains in solution as manganous chloride $MnCl_2$.

Sulphur is oxidized, and passes into solution as yellow ferric sulphate $Fe_3(So_4)_3$.

Phosphorus is oxidized, and remains dissolved as ferric phosphate $FePO_4$.

Arsenic is converted into arsenic acid, and on evaporation to dryness some liquid chloride $AsCl_3$ is formed, which vaporizes and escapes.

Tungsten is oxidized, being partly converted into insoluble yellow WO_3, and partly into the hydrated acid H_2WO_4, which passes into solution.

Chromium is dissolved to green chromic chloride $CrCl_5$. If, however, a considerable percentage of the element is present an insoluble metallic residue, rich in chromium, remains unacted upon by the acids.[2]

Nickel passes into solution as $NiCl_2$.

[1] Brodie has shown that nitro-sulphuric acid acts appreciably upon graphite, forming a compound which, when ignited, gives off oxygen, hydrogen, and sulphuric anhydride SO_3, leaving a finely-divided residue of pure graphite.

[2] This metallic residue is usually free from sulphur and phosphorus.

Aluminium is dissolved, forming colourless aluminic chloride $AlCl_3$.

Copper passes into solution as green cupric chloride $CuCl_2$.

Titanium passes into solution as colourless titanic acid H_4TiO_4.

A careful study of the foregoing reactions will give to the student a good idea why a certain acid should be used in the first stage in the estimation of a certain element, and yet must be carefully avoided in the preliminary solution having for its object the determination of some other element.

The Estimation of Silicon.

In the literature of iron and steel analysis it may be often noticed, that the authors insist very strongly on the necessity in making an estimation of silicon of determining how much exists as Si combined with the iron, and how much as SiO_2 in the involved slag. In modern well-fused steels, except locally, and as the result of some accidental and abnormal circumstance, there is practically no slag. In high-class wrought irons, such as Lancashire hearth Swedish rolled bars, there are found under the microscope formidable-looking streaks of dark cinder; yet, when the iron is analyzed, the total silicon will be found to be about 0·02 %. In low grade English bars, however, the slag is present in much larger quantities: certain sections under the microscope appear indeed to contain more slag than iron. It may be that occasionally, for research purposes, an estimation of the slag (and its composition) in wrought iron is required, but from an every-

day, practical point of view the subject may be at once dismissed. There is an analytical tradition to the effect that when iron containing silicon in combination is dissolved in strong hydrochloric acid, some silicuretted hydrogen gas SiH_4 is evolved, and that consequently the results are liable to be low. It is therefore usually deemed necessary for the determination of silicon to employ either aqua regia or nitro-sulphuric acid as a preliminary solvent, in order to prevent the formation of SiH_4. These precautions knock down a man of straw, as the evolution of SiH_4 is a myth. The results given by the aqua regia process and by Drown's nitro-sulphuric method are quite accurate, but the evaporation takes longer, and the fumes are more irritating than when HCl is used. The author some years ago, by means of triplicate estimations on many samples of steel occurring in ordinary laboratory practice, proved the results obtained by the three methods to be identical, but at his request Mr. Andrew MacWilliam and Mr. Dixon Brunton undertook and carried out at the Sheffield Technical School a very interesting research upon this point on specially selected steels. The results obtained are so instructive that the author has tabulated the most interesting from the *Journal of the School Metallurgical Society*. (Table I., p. 65.)

TABLE II.—HIGH SILICON STEEL.

No.	Grammes of Steel.	Solvent.	Weight of SiO_2.	Si %.
1	3	HCl	0·2768	4·306
2	3	,,	0·2788	4·337
3	3	aqua regia	0·2749	4·276
4	3	,, ,,	0·2784	4·331

A final attempt was made to evolve SiH_4 from the

TABLE I.—STEEL FOR CASTINGS.

Experiment No.	Grammes of Steel taken.	Solvent.	Weight of SiO_2.	% Silicon.	Remarks.
1	3	35 cc. Hydrochlorie acid, sp. gr. 1·16.	0·0202	0·314	Evaporated to dryness, re-dissolved in 25 cc. HCl, sp. gr. 1·16, and 50 cc. of water.
2	3		0·0203	0·316	
3	3	35 cc. Aqua Regia.	0·0201	0·313	Same treatment as Nos. 1 and 2.
4	3		0·0200	0·311	
5	3	30 cc. HNO_3, sp. gr. 1·20. 20 cc. H_2SO_4, sp. gr. 1·80. 20 cc. of water.	0·0204	0·317	Evaporated until copious white fumes were evolved, and then diluted and boiled with water.
6	3		0·0205	0·319	
7	3	20 cc. H_2SO_4, sp. gr. 1·80. 60 cc. of water.	0·0203	0·316	Same treatment as Nos. 5 and 6.
8	3		0·0206	0·320	
9	3	35 cc. HNO_3, sp. gr. 1·20.	0·0010	0·016	Same treatment as Nos. 1 and 2.
10	3		0·0011	0·017	

high silicon steel under specially favourable conditions. The hydrochloric acid was allowed to act upon the drillings in the cold for eighteen hours in an atmosphere of hydrogen: the evolved gases were passed through aqua regia to oxidize any SiH_4 given off to silicic acid. The silicon in the flask in which the steel had been treated, and that present in the aqua regia, were then estimated in the usual manner with the following results:—

Weight in grammes of		Si %
SiO_2 in flask	0·2713	4·223
SiO_2 in aqua regia	0·0010	0·016
Total	0·2723	4·239

The foregoing series of experiments conclusively prove that no silicon is evolved as SiH_4 when steel is dissolved in hydrochloric acid solution.

The Process.

(Time occupied, about 3 hours.)

Weight taken.—Weigh out 4·67 grammes of drillings into a 20-oz. beaker.

Dissolving.—Put on the cover, and add down the lip 50 cc. of strong hydrochloric acid solution. Place the beaker on the hot plate, and heat quietly until the steel is dissolved; then, still keeping on the cover, boil briskly till the acid becomes quite thick with precipitated ferrous chloride. To hasten the analysis the boiling should be kept up as long as no spitting occurs, and the drops of condensed acid from the underside of the cover do not endanger the safety of the beaker by falling upon the hot bottom and cracking it.

Evaporating to dryness.—Next, remove the beaker to a cooler part of the plate, take off the cover and place it, concave side downwards, on an earthenware filter-drier. Gradually increase the heat under the beaker, carefully avoiding spitting, till the mass is quite dry. Remove the hot vessel from the plate, and *hold it in the hand till fairly cool:* if the heated beaker is at once placed in contact with the comparatively cold bench it will probably crack.

Re-dissolving.—When cool, replace the cover (nothing having been lost from its under surface), and add to the dry chlorides enough strong hydrochloric acid solution to thoroughly saturate them (an excess does no harm). Heat for a few minutes with the strong acid till the chlorides have lost any red appearance; then add about 75 cc. of water, and boil well till every particle of chloride of iron is dissolved.

Filtering.—Next collect the precipitate of silica on an ashless filter-paper, contained in a 2¼-in. ribbed funnel supported on a conical beaker. First of all, rinse the underside of the cover into the filter, if necessary using a policeman to detach any adhering splashed-up particles of silica; then pour through the solution, thoroughly wash out the beaker, after going over the whole of the inside with the policeman of course, finally, carefully washing any silica adhering to the latter on to the filter-paper. All the washing must be done with cold water.

Washing.—Now comes the point at which most students at first go wrong in estimating silicon. *Every trace of iron salt must be washed from the filter-paper.* It is not sufficient that no yellow tinge is noticeable, the paper must be washed repeatedly and alternately with hot dilute HCl, and cold water. The former may be heated in

a beaker, and should be poured round the *edges* of the filter by means of a glass rod; also direct the wash-bottle jet upon the edges of the paper: if these are well washed the rest of the filter and the silica will take care of themselves. Finally, thoroughly wash with cold water.

Drying.—As soon as the last washings have passed through, carefully transfer the paper from the funnel to a filter-drier, and heat on the plate till quite dry.

Igniting.—Then fold it up and place in a clean, carefully-weighed platinum crucible which has been recently ignited and allowed to cool in the desiccator. The tared cover of the crucible may be left in the balance-case. Ignite the crucible and its contents in the muffle till the silica is *snow white.*

Weighing.—Allow the crucible to cool in the desiccator, put on the cover, and carefully re-weigh. The increase over the original weighing is SiO_2, containing 46·7 % Si. The weight of the silica multiplied by 10 gives the percentage of silica in the steel.

Methods for Special Steels.

The foregoing process is not applicable to tungsten steels, a method for which is given on p. 133.

In the case of chrome steels, it often happens that after carrying out the above method the silica is not white, owing to the presence of a little oxide of chromium. This should be separated by adding to the crucible containing the impure SiO_2 about 2 grammes of pure acid potassium sulphate $KHSO_4$;[1] the latter is cautiously heated till fused, then more strongly, till white fumes of sulphuric acid are

[1] For the preparation of this salt see p. 239.

given off; when cold, the mass of potassium sulphate is dissolved out with dilute hydrochloric acid, and the purified silica is filtered off, washed, dried, ignited, and weighed exactly as before described.

Theory of the Process.

The hydrochloric acid, as already shown (p. 57), converts the silicon into silicic acid. In steels containing much over 0·1 % of silicon, some of the silica will be noticed on the surface of the liquid and sides of the beaker as a yellowish scum. The yellow coloration is due to the air in the beaker bringing about a conversion of a little of the pale-green solution of ferrous chloride with which the particles are saturated into yellow ferric chloride, thus—

$$6\ FeCl_2 + 6\ HCl + 3\ O = 6\ FeCl_3 + 3\ H_2O$$

On evaporating to dryness, more ferric chloride is formed, whilst the silica is dehydrated and rendered quite insoluble in acids and water, thus—

$$H_4SiO_4 = SiO_2 + 2\ H_2O$$

On re-dissolving the chlorides of iron and manganese, and also the phosphorus salts present, the silica, together with a small quantity of combined carbon which has not been evolved as hydrocarbon, and any graphite present, remains suspended in the liquid. The carbon communicates to the silica a dirty appearance, but, on being burnt off, leaves it a snow-white powder. If the residue has a reddish tinge or a deep, red-brown ring of Fe_2O_3 round it, the filter-paper has not been properly washed. If the ignition has not been strong enough, the precipitate may be grey with carbon, especially in steel containing graphite which requires a prolonged burning.

In weighing the precipitate, it should be always remembered that SiO_2 *is very hygroscopic*, and unless proper precaution is taken, absorbed aqueous vapour may cause the result to be recorded higher than is actually the case.

The reason for taking 4·67 grammes of steel is to do away with any calculation. This weight is $\frac{1}{10}$ the amount of *Si* contained in 100 parts of SiO_2, hence the weight of $SiO_2 \times 10 = \%\ Si$.

As a rule, the ashless filters of the size used in a $2\frac{1}{4}$-in. funnel leave a negligible residue: if not, $\frac{1}{5}$ the weight of the residue left by igniting five papers in the same packet as the filter used, must be deducted from the weight obtained.

Model of Record.

22 Jan. '84. Axle Steel. Blow No. 124.

Weight taken 4·67 grammes.

Weight of crucible and cover + SiO_2 + ash	31·6327
Weight of crucible and cover	31·6263
	0·0064 = SiO_2 + ash.

$$
\begin{array}{rl}
 & \cdot 0064 \\
- & \cdot 0006 \text{ weight of filter ash.} \\
\hline
\text{Grammes } SiO_2 & \cdot 0058 \times 10 = 0\cdot 058\ \%\ Si.
\end{array}
$$

Or

$$
\begin{array}{r}
\cdot 0058 \\
46\cdot 7 \\
\hline
3736 \\
2335 \\
\hline
4\cdot 67)\cdot 27086(0\cdot 058\ \%\ Si \text{ as above.} \\
2335 \\
\hline
3736 \\
3736 \\
\hline
\cdots\cdots
\end{array}
$$

The reactions taking place during the purification of the silicon contaminated with Cr_2O_3 are as follow: the acid sulphate on heating strongly forms the normal sulphate, and gives off sulphuric acid thus—2 $HKSO_4 = K_2SO_4 + H_2SO_4$; the latter in contact with the oxide of chromium at a comparatively high temperature converts it into soluble chromic sulphate, thus—

$$Cr_2O_3 + 3\ H_2SO_4 = Cr_2(SO_4)_3 + 3\ H_2O$$

The silica is left mechanically mixed with the mass of sulphates, and the latter, being quite soluble in dilute hydrochloric acid, are dissolved whilst the insoluble SiO_2 remains as a white residue.

Gravimetric Determination of Manganese.

(Re-agent required $(C_2H_3O_2)NH_4$.)

Preparation.—A strong solution of ammonium acetate is best made in the following manner:—Place in a 40-oz. beaker 100 cc. of pure liquid ammonia 880, and add to it the British Pharmacopeia solution of acetic acid containing about 33 % of true $C_2H_4O_2$ till the liquid, after thoroughly stirring, turns blue litmus paper red: a volume of acid several times greater than that of the ammonia will be required. Preserve the solution in a well-stoppered bottle. It should be colourless, and form no dark deposit: if the latter precipitates the re-agent is not fit to use, the acid having been impure with tarry matter, which may seriously interfere with the sharp separation of the manganese from the iron. The reaction taking place between the ammonia and the acetic acid is as follows:—

$$NH_4HO + C_2H_4O_2 = Am(C_2H_3O_2) + H_2O$$

Ammonium hydrate and acetic acid yield ammonium acetate and water.

The Ammonium Acetate Process.

Mr. A. A. Blair, in his admirable compilation of the various methods proposed for iron and steel analysis, remarks that the acetate method for the determination of manganese is tedious, and for low manganese steels, objectionable on account of the fact that only one gramme of the steel can be conveniently operated upon.

There is no doubt that if it were necessary to go through the series of chemical gymnastics advocated by Mr. Blair, the acetate method would be found to be extremely tedious, but fortunately for steel analysts, such necessity does not exist. As a matter of fact, an accurate determination of the manganese in 2 or 3 grammes of steel can be readily made by the acetate process in about four hours.

The Method.

Weight taken.—For ordinary steels weigh out into a 40-oz. beaker, marked on the side at 450 cc., exactly 2·4 grammes of steel.

Dissolving.—Cover the beaker, and add down the lip 50 cc. of fuming hydrochloric acid. Very quietly boil the liquid on the hot plate till the steel has dissolved, then add 3 cc. of strong nitric acid (sp. gr. 1·43); boil for two minutes, and dilute with hot water to the 450 cc. mark.

Neutralizing.—Heat the liquid to incipient boiling, remove the cover, rinsing the liquid upon its underside into the beaker, next add to the solution dilute liquid ammonia[1] little by little, and finally drop by drop, with

[1] Made by adding 25 cc. of cold distilled water to the same volume of 880 ammonia solution.

constant stirring till the solution has become much darker in colour, and a faint, permanent precipitate has produced a slight turbidity. Carefully avoid over-shooting this point by a too rash addition of ammonia. The above neutralization must be carried out with great care, the liquid being well stirred at a nearly boiling heat with a glass rod after each addition of ammonia till the precipitate at first formed is re-dissolved, being also careful to work down into the solution any precipitate which may adhere to the sides of the beaker.

Precipitating the iron.—Next add 50 cc. of *cold* ammonium acetate solution little by little, with constant stirring, then wash and remove the glass rod, replace the cover, and gradually bring the contents of the beaker to a full boil, which should be maintained for two minutes but not more, then remove from the plate.

Filtering.—Take off the cover, let it drain into the beaker, and place it concave side downwards on an earthenware filter-drier. Pour the solution and bulky, dark red-brown precipitate into a clean flask, graduated at the lower part of the neck for 605 cc.; well wash the cover and beaker with hot water, of course adding the washings to the liquid in the graduated flask; next by means of the wash-bottle jet dilute the liquid with hot water to about 605·5 cc., and render the whole mass thoroughly homogeneous by stirring with a thermometer. As the liquid cools, withdraw the thermometer just clear of it from time to time, till, after the thermometer has drained, the meniscus of the fluid is coincident with the 605 cc. mark. *Note the temperature*, and remove the thermometer without washing. Now support over a dry flask, graduated low down in the neck at 500 cc., a 5-in. ribbed funnel containing a *dry* filter of thick German paper, the edges of which are

$\frac{1}{8}$ in. below those of the funnel: the latter should also be provided with a 6-in. diameter cover. Pour the liquid and precipitate very gently at first upon the filter, and allow rather less than 500 cc. to pass through. The glass cover should, as far as possible, be kept on the funnel during the filtration to prevent undue evaporation. The precipitate and the unfiltered fluid may now be thrown away. Place the 500 cc. flask on the heating plate and put it in a clean dry thermometer, and raise the temperature to that previously noted; throw out the slight excess of liquid with the thermometer, till, on withdrawing the latter the meniscus of the liquid registers exactly 500 cc. at the original temperature.

Evaporating the filtrate.—Pour the clear or very faintly yellow liquid into a 40-oz. beaker, carefully washing out the flask with hot water, and adding the washings to the main quantity. Next boil down the contents of the beaker either briskly with the cover on, or quietly with the cover off, to about 250 cc.

Removal of traces of iron.—Filter the evaporated liquid, in which may be suspended a small brown precipitate, through a 2-in. ribbed funnel into a 30-oz. registered flask; carefully rinse out the beaker with hot water, and well wash the filter paper with the same; remove the funnel, and thoroughly cool the *crystal clear* liquid by immersing the flask in a trough of cold water, or allowing a stream from the tap to play upon the flask whilst the liquid is shaken round.

Precipitating the manganese.—When cold, add 4 cc. of pure bromine, and give to the liquid a circular motion till only 2 or 3 small drops of bromine remain undissolved, and the solution has a somewhat deep, reddish-brown colour. Next add quietly 30 cc. of 880 liquid ammonia,

shake the liquid cautiously round, and place the flask on the hot plate, keeping its contents just short of boiling till the liquid is crystal clear, and the dark-brown precipitate has gathered into rapidly settling flocks.

Filtering off the precipitate.—Collect the precipitate on an ashless filter contained in a 2-in. ribbed funnel; see that every particle is washed out of the flask, if necessary calling in the aid of a long policeman to detach any adhering film or flocks. Wash the paper and its contents thoroughly with hot water, allow to drain, and dry it in the manner already described for the estimation of silicon (see p. 68).

Igniting and weighing.—When quite dry fold the filter and place it in a platinum crucible, previously carefully ignited, cooled and tared, and strongly ignite in a gas muffle for 15 minutes. Allow the crucible to go quite cold in the desiccator and re-weigh. The increase is due to Mn_3O_4 containing 72% of metallic manganese. The calculation must be made on the basis that the steel containing the manganese weighed 2 grammes. The colour of the precipitate should be a not very deep red-brown: it should be powdery, and free from any lumpy appearance, otherwise oxide of iron is probably present. As Mn_3O_4 is not hygroscopic, it may, without sensible error, be carefully brushed out of the crucible on to the foil of the balance-pan and weighed direct.

Colorimetric Estimation of Ferric Oxide in the Manganese Precipitate.

If any doubt exists as to the purity of the precipitate from F_2O_3 (or if it has not been deemed necessary to evaporate the filtrate containing the manganese to half

bulk), the latter should be tested for, and if present, estimated colorimetrically, the weight found being of course deducted from that of the Mn_3O_4.

Standard iron solution.—Make a standard solution of ferric chloride by dissolving in a small covered beaker 0·0701 gramme of clean drillings of pure Swedish bar iron (containing 99·8 % *Fe*) in 15 cc. strong *HCl*. When the metal is in solution add to the ferrous chloride 3 *drops* of nitric acid, sp. gr. 1·43. Briskly boil the ferric chloride for a few minutes, and then gently evaporate it to very low bulk, dilute and transfer every trace of the iron solution from the beaker and cover into a 1000 cc. flask, and fill to the mark with distilled water. Next pour the litre of liquid into a large beaker, which must be clean and quite dry; stir thoroughly with a glass rod, and pour back into the flask: by this treatment a homogeneous liquid is obtained corresponding to 0·0001 gramme of Fe_2O_3 in each cc. It should be transferred to a well-stoppered bottle, and its strength legibly labelled.

Estimation of the iron.—Brush the manganese precipitate into a small beaker, put on the cover, add a few cc. of strong *HCl* to dissolve the precipitate, and boil briskly. If any appreciable quantity of iron is present, the solution will have a yellow colour: quietly evaporate off most of the acid, and dissolve up the semi-dry chlorides in 2 cc. of water. Drain the solution into a 20 cc. graduated tube, rinse out of the beaker and add to the main liquid every trace of chloride solution, using altogether about 6 cc. of water at three times. Now add to the tube 1 cc. of a *colourless* solution of sulphocyanide of ammonium containing about 5 % of the salt;[1] add distilled water to 10 cc., and thor-

[1] An excess must be avoided, as it destroys the colour; on the other hand, too little fails to develop the full tint.

oughly mix the contents of the tube. If much iron is present the liquid will be blood-red in colour, and even if mere traces of iron are contained in the manganese precipitate, a pinkish tinge will be developed. The student with a little experience will be able to judge at once, roughly, the weight of oxide of iron present. If, as is generally the case, only a moderate colour is produced, deliver from a 20 cc. burette graduated in tenths into another graduated 20 cc. tube exactly 1 cc. of the standard iron solution; add 8 cc. of water and 1 cc. of the sulpho-cyanide solution, mix well, and compare the tints of the liquids in the two tubes in the manner already described on p. 51 for the estimation of carbon by colour. If the standard is the darker, the oxide of iron present may be ignored, being under $\frac{1}{10000}$ of a gramme; if the tints are equal the oxide weighs that amount; if, however, the standard is lighter than the solution of the precipitate, make up a fresh standard, taking 2 cc. of the iron solution, 7 cc. of water, and 1 cc. of sulphocyanide solution. If the standard is still too light, make up fresh standards, advancing by $\frac{1}{10000}$ of a gramme of oxide till the required coincident tint is obtained. The last standard will be made up of 9 cc. of iron and 1 cc. of sulphocyanide solution, giving a colour corresponding to 0·0009 gramme of ferric oxide, or a + error of 0·032 % manganese on 2 grammes of steel. When such an error is approached it is indicative of some violation by the student of the instructions previously given. It may, however, be due to the use of impure re-agents, introducing during the analysis organic substances other than acetates which have prevented the complete separation of the iron. With pure re-agents and skilful manipulation the amount of F_2O_3 seldom exceeds 0·0002 gramme, or a + error of 0·007 % *Mn*.

The reaction taking place between the ferric chloride and the ammonium sulphocyanide (or thiocyanate) is as follows:—

$$\underset{\text{Yellow}}{FeCl_3} + \underset{\text{Colourless}}{3\ AmSCy} = \underset{\text{Blood-red}}{Fe(SCy)_3} + \underset{\text{Colourless}}{3\ AmCl}$$

Ferric chloride and ammonium thiocyanate yield ferric thiocyanate and ammonium chloride.

Model of Record and Calculation of Result.

Feb. 2, 1884.

Estimation of manganese in open-hearth steel drillings marked *SH.* Weight of steel taken 2·4 grammes.

$$\begin{array}{rr}
\text{Crucible} + Mn_3O_4 = & 29{\cdot}6467 \\
\text{Weight of crucible} = & \underline{29{\cdot}6283} \\
 & {\cdot}0184 \\
-\ \text{ash} & \underline{{\cdot}0003} \\
 & {\cdot}0181 \\
-\ Fe_2O_3 \text{ by colour} & \underline{{\cdot}0002} \\
Mn_3O_4 = & {\cdot}0179 \\
 & \underline{72} \\
 & 358 \\
 & 1253 \\
 & 2)\overline{1{\cdot}2888} \\
 & \underline{\underline{0{\cdot}644}}\ \%\ Mn.
\end{array}$$

Theory of the foregoing Modification of the Acetate Process.

The author long ago discarded the use of nitric acid for the preliminary solution of the steel. This acid, which possesses the advantage of at once yielding the iron in the ferric condition, also brings into solution the brown organic matter containing the carbon. This, when present in some quantity, as in the case of tool steel, has a decided

tendency to prevent the complete precipitation of the iron, retaining a small quantity in solution till the final precipitation of the hydrate of manganese with bromine and ammonia; it will then of course be found with the ignited Mn_3O_4 as F_2O_3.

The nitric acid added to the solution of *ferrous* chloride oxidizes (chlorinizes) it to *ferric* chloride, thus—

$$FeCl_2 + HNO_3 + HCl = FeCl_3 + H_2O + NO_2$$

Pale-green ferrous chloride, nitric and hydrochloric acids yield yellow ferric chloride, water, and the deep brown gas, peroxide of nitrogen. The manganese remains as *manganous* chloride $MnCl_2$, and an indispensable condition for the process is, that no ferrous chloride must be present, *because ferrous acetate is soluble in water acidulated with acetic acid.* During the neutralization with ammonium hydrate, the free hydrochloric and nitric acids are converted respectively into neutral ammonium chloride and nitrate, thus—

$$HCl + AmHO = AmCl + H_2O$$
$$HNO_3 + AmHO = AmNO_3 + H_2O$$

On the addition of ammonium acetate, the iron is precipitated as an indefinitely constituted mixture of ferric acetate and hydrate [$x\ Fe_2(C_2H_3O_2)_6 + y\ Fe_2(Ho)_6$], generally known as basic ferric acetate, and some free acetic acid is liberated. The complex reactions bringing about this result are not clearly known, but the precipitate with variations in composition varies in appearance; three different types must be mentioned—

1. A rather dark red-brown precipitate, which settles fairly rapidly and filters moderately quickly, the filtrate being clear and colourless.

2. A slimy precipitate of a yellowish red-brown colour, which filters very slowly, the filtrate being often coloured.

3. A rapidly subsiding brick-dust coloured precipitate, the finely-divided portions of which usually pass through the pores of the paper with the filtrate.

The first-mentioned precipitate is the one the student should always endeavour to obtain. Its formation indicates a sharp separation of the iron and manganese, and proves that the neutralization has been successfully performed. If the practical instructions already given are carefully carried out, the second and third highly objectionable forms of precipitate will not be obtained. When, however, some accidental departure from the conditions under which the analysis should be made results in the production of either of these modifications of basic ferric acetate, it is always advisable to start the analysis again, and obtain the proper precipitate.

The object of evaporating the solution containing the manganous acetate to half its original bulk, is to ensure the precipitation of any iron present in the filtrate. A small quantity sometimes remains dissolved with the manganese, but is thrown down during the second boiling. The bromine is added as an *oxidizing agent* to convert the manganous into manganic hydrate at the moment of its precipitation with ammonia. Manganous hydrate $Mn(HO)_2$ *is soluble in ammonium salts;* manganic hydrate $Mn_2O_2(HO)_2$, however, is *quite insoluble* in their presence, and is therefore completely precipitated thus—

1. $(C_2H_3O_2)_2Mn + 2\ AmHO = Mn(HO)_2 + 2\ (C_2H_3O_2)Am$. Manganous acetate and ammonium hydrate yield manganous hydrate and ammonium acetate.

2. $2\ Mn(HO)_2 + 4\ Br + 2\ H_2O = Mn_2O_2(HO)_2 + 4\ HBr$. Manganous hydrate, bromine, and water yield manganic hydrate and hydrobromic acid.

The last-named is of course neutralized by the excess of ammonia present, thus—

3. $HBr + AmHO = AmBr + H_2O$. Hydrobromic acid and ammonium hydrate yield ammonium bromide and water.

Of course these three reactions take place practically simultaneously, and it will be observed that the bromine acts as an oxidant by decomposing water, combining with the hydrogen, and liberating the (nascent) oxygen.

The use of a fixed alkali, namely, sodium carbonate for neutralizing and sodium acetate for precipitating, has been insisted upon as being absolutely necessary to ensure success, because the manganic hydrate is alleged not to be completely precipitated in the presence of large quantities of ammonium salts. As a matter of fact, the employment of ammonium compounds is attended by several advantages over the use of sodium salts, which, in the author's opinion, produce instead of prevent error. Where possible, precipitations from solutions of the fixed alkalies should always be avoided; there is little doubt that the belief in the partial solubility of manganic hydrate in ammonium chloride and bromide arose through chemists accepting, without personal investigation, the statement of Fresenius to that effect.

The ignition should be made with the lid off the crucible, in a *hot* muffle furnace, and be continued for ten minutes after the filter-paper has all been burned off, otherwise the residue may not strictly conform to the formula Mn_3O_4, which, under the above conditions, it will possess.

Only one other point remains to be explained. The student, having made even one estimation of manganese, will readily appreciate the difficulty of washing the large

iron precipitate till free from manganese, and also the time that will be thus lost. In the instructions given, this difficulty has been entirely done away with by taking only $\frac{5}{6}$ of the filtrate; the manganese in the 2·4 grammes of steel taken for analysis was obtained in a solution of known temperature occupying at that temperature 600 cc. (The extra 5 cc. form a correction for two small sources of error, first, the volume of the precipitate itself; second, the slight concentration of the hot liquid from evaporation during filtration.) Therefore, in 500 cc. of the liquid at a like temperature, equalling $\frac{5}{6}$ of the total volume, there will be contained the manganese present in $\frac{5}{6}$ of the weight of steel originally taken, and $\frac{5}{6}$ of 2·4 grammes = 2 grammes.

There is no necessity in estimating manganese in ordinary steel to precipitate the iron twice, or indeed, as one author recommends, three times. The method just dealt with gives, with a little practice, remarkably sharp separations, as will be seen from the following table, embodying results (extracted from the author's note-book) obtained on various steels by single and double precipitations of the iron :—

Blow No. or mark.	% Manganese by single precipitation.	% Manganese by double precipitation.	
418	0·684	0·684	=
419	0·745	0·763	+ ·019
420	0·710	0·710	=
SCX	0·634	0·634	=
SH	0·644	0·655	+ ·011
124	1·364	1·357	− ·007

Estimation of Manganese in Special Steels.

Nickel and copper.—If the steel in which the manganese is being determined contains nickel or copper, a portion of the last-named metals will pass into the filtrate containing the manganese, and although the hydrates of nickel and copper are both soluble in ammonia, small percentages are nevertheless very liable to be carried down with the manganese precipitate: to prevent the possibility of this, pass through the boiling manganese filtrate (at that stage when it has been concentrated to 250 cc. to throw down the last traces of iron) a brisk current of washed sulphuretted hydrogen from a Kipp's apparatus for five minutes. The nickel and copper are completely precipitated as black sulphides NiS and CuS. These are filtered off along with the previously precipitated residue of iron, and are well washed with water containing a little H_2S in solution. The manganese in the filtrate is then precipitated in the usual manner with bromine and ammonia.

High silicon, tungsten, and graphite.—When these substances are present, they remain suspended in the solution, and may interfere with the accurate determination of the exact point at which the liquid is neutralized: it is therefore advisable to commence the analysis on 2·88 grammes of drillings, and after the oxidation of the hydrochloric acid solution of the steel with nitric acid, to evaporate the liquid to about 10 cc., and then to transfer it without loss to a 60 cc. flask; dilute to the mark when cold, mix the liquid thoroughly, and filter off through dry paper contained in a 2-in. funnel 50 cc. of the liquid into a dry marked flask. This 50 cc. of solution will contain $\frac{5}{6}$ of 2·88

or 2·4 grammes of steel. It is transferred without loss to the marked 40-oz. beaker, diluted to 450 cc., and the analysis proceeded with as usual.

Chromium and aluminium.—These elements, although their hydrates and acetates are under ordinary circumstances soluble in free acetic acid, are, under the conditions present during the estimation of manganese, completely carried down with the iron precipitate, as the author has never found them present in the residue of Mn_3O_4.

VOLUMETRIC ESTIMATION OF MANGANESE. (Ford and Williams, modified.)

(Time occupied, about 1 hour.)

Re-agents required.

Pure iron.—This must be obtained in the form of clean drillings from Swedish Lancashire hearth bar, preferably of the brand known as "little S," which is manufactured from the middle bed Dannemora ore, and usually contains 99·8 % of iron.

Dilute solution of $K_6(C_3N_3)_4Fe_2$.—Dissolve one *small* fragment of this salt (usually known as red prussiate of potash, or potassium ferricyanide) in 10 cc. of distilled water. This solution should be freshly made for each set of indications.

Standard solution of $K_2Cr_2O_7$.—Dissolve 1·7845 grammes of pure, dry, selected crystals of potassium bichromate in about 250 cc. of hot water contained in a 20-oz. beaker. When cold, carefully transfer the solution without the smallest loss into a clean litre flask; dilute exactly to the mark with cold distilled water, and mix the contents of

the flask till perfectly homogeneous. Store this solution in a well-stoppered bottle, and label it "100 cc. = 0·2036 gramme *Fe*, or 2 % *Mn* on 5 grammes of steel."

The Process.

Dissolving.—Dissolve 5 grammes of drillings weighed out into a 20-oz. covered beaker in 60 cc. of nitric acid, sp. gr. 1·2, and quietly boil down to about 30 cc.

Precipitation of MnO_2.—Next add 10 cc. of nitric acid, sp. gr. 1·43, and then very cautiously 5 grammes of pure, dry, powdered chlorate of potash ($KClO_3$), boil for a few minutes (of course with the cover on), and twice more repeat the treatment with strong nitric acid and potassic chlorate, thus using altogether 30 cc. of HNO_3 and 15 grammes of $KClO_3$. After the last addition boil well, remove from the plate, dilute with 75 cc. of hot water, and shake round the contents of the beaker.

Filtering.—Allow the precipitate to settle somewhat, and then collect it upon a 110 mm. pure filter contained in a 2¼-in. funnel, detaching as far as possible every particle of adhering precipitate from the sides of the beaker by means of a policeman. It sometimes happens that a ring composed of a thin film of precipitate defies removal: the weight of this, however, is so minute that it may be ignored without sensible error. The precipitate and filter paper must now be thoroughly washed with hot water till quite free from nitric acid, and the drops from the stem of the funnel will no longer turn blue litmus paper red.

Titrating.—When weighing out the steel for analysis, there should also be weighed out into a perfectly clean, dry 10-oz. flask 0·204 gramme of the Swedish iron drillings, and about the time the washing of the precipitate is

commenced, add to the flask 70 cc. of dilute sulphuric acid (1 in 7), place a watch-glass on the flask, and boil on the hot plate till the last particle of iron is dissolved. Then remove the flask and rinse the drop from the underside of the watch-glass. Next fold the filter containing the brown precipitate, and cautiously drop it bodily down the neck of the flask into the iron solution. Shake the liquid round once or twice till the whole of the precipitate has dissolved and only white filter paper remains.

Fill up a 50 cc. burette, graduated in tenths, and carefully set the meniscus of the liquid at zero. The standard solution is then run into the flask till the whole of the ferrous sulphate is oxidized. The exact point at which this occurs is determined by the indicator solution of ferricyanide. Two or three rows of small drops of the latter are placed upon a glazed white porcelain slab by means of a glass rod. As long as any unoxidized iron remains in the flask, a drop of the liquid withdrawn on a glass rod and placed on the slab close to a drop of ferricyanide solution will, on the two drops being allowed to mingle, produce a blue coloration, which fades in intensity as the final point is approached. As soon as this happens, not more than half a cc. of bichromate solution should be added between each trial. In deciding when the iron solution has ceased to re-act with the indicator, it must be recollected that the chromic sulphate produced in the reaction has itself a greenish tint, so that a drop of the liquid *per se* should be compared on the slab alongside the drop mixed with ferricyanide. It should also be remembered, that when the proportion of ferrous salt becomes very small, the colour is not developed for perhaps half a minute. With a little practice, it will be found much easier to carry out the foregoing titration than to describe it.

If under 1 °/₀ of manganese is present in the steel under examination, the burette after the meniscus of its contents has been run down exactly to the 50 cc. mark, will require re-filling, and the amount of iron prescribed is only capable of registering a maximum of 2 % of manganese, which of course more than meets the case of ordinary steels. *The student should be very careful after each addition of bichromate to shake the flask round so as to thoroughly mix the liquids.*

Reading off the percentage.—Subtract the number of cc.s used from 100: each cc. of the remainder equals ·02 % of manganese, therefore, remainder × ·02 = % *Mn.*

Examples.

1. 34 cc. of bichromate solution were required.
   Then 100 — 34 = 66, and 66 × ·02 = 1·32 % *Mn.*
2. 87·5 cc. of bichromate solution were required.
   Then 100 — 87·5 = 12·5, and 12·5 × ·02 = 0·25 % *Mn.*

Theory of the Foregoing Method.

The fact that in a strong nitric acid solution manganous nitrate is, by a complex reaction, oxidized to insoluble manganese dioxide on the addition of $KClO_3$ was first noticed by Hannay. The peroxide of manganese precipitate is, however, contaminated with basic iron and potash salts, and hence cannot be weighed direct. On dissolving the precipitate in a solution of ferrous sulphate containing an excess of free sulphuric acid, the following reaction takes place:—

$$\underset{(55)}{MnO_2} + 2\,\underset{(56)}{FeSO_4} + 2\,H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2\,H_2O$$

Peroxide of manganese, ferrous sulphate, and sulphuric acid yield manganous sulphate, ferric sulphate, and water. It is therefore evident that 55 (55 × 1) parts by weight of manganese in the form of dioxide, oxidize 112 (56 × 2) parts by weight of ferrous iron into ferric iron. If a known weight and an excess of ferrous iron is present, it is evident that if the unoxidized excess can be accurately determined the amount of iron oxidized by the manganese will then be known, and consequently the weight of the manganese itself. The excess of ferrous iron is estimated by observing how much $K_2Cr_2O_7$ is required to oxidize it according to the following reaction (Penny's process)—

$$\underset{(39)}{K_2}\,\underset{(52)(16)}{Cr_2O_7} + 6\,\underset{(56)}{FeSO_4} + 7\,H_2SO_4 = 3\,Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7\,H_2O$$

Potassium bichromate, ferrous sulphate, and sulphuric acid yield ferric, chromic, and potassic sulphates and water. 294 (78 + 104 + 112) parts by weight of $K_2Cr_2O_7$ oxidize 336 (56 × 6) parts of iron from the ferrous to the ferric condition; the weight of iron used is found thus—

Required the weight of iron which 2 °/ₒ of manganese in 5 grammes of steel will oxidize.

2 °/ₒ of 5 grammes $= \frac{5 \times 2}{100} = 0{\cdot}1$ gramme of *Mn*.

Then if 55 parts of *Mn* oxidize 112 parts of *Fe*
0·1 „ „ „ x „ „ $\Big\}\ \frac{112 \times {\cdot}1}{55} = 0{\cdot}2036$ gr. *Fe*.

But the iron employed contains 99·8 % *Fe*.

Hence if 98·8 = ·2036
100·0 = x $\Big\}\ \frac{{\cdot}2036 \times 100}{98{\cdot}8} = 0{\cdot}204$ gramme *Fe*.

That is to say, 0·204 gramme of the slightly impure iron is equivalent to 0·2036 gramme of chemically pure metal.

Then if 336 parts of *Fe* require 294 parts of $K_2Cr_2O_7$
0·2036 „ „ „ x „ „

$$\frac{294 \times {\cdot}2036}{336} = 0{\cdot}178125 \text{ gramme of } K_2Cr_2O_7$$

This weight (dissolved in 100 cc.) is equal in oxidizing power to 0·1 gramme of manganese in the form of MnO_2;

for 1000 cc. ten times the weight would be required, or 1·7813 grammes. The accuracy of the solution should be proved by titrating 0·204 gramme of Swedish iron dissolved in excess of H_2SO_4 in the manner already described; exactly 100 cc. should be required to complete the oxidation. If, however, the solution is too strong, the required quantity of water to adjust it is calculated; if too weak, the necessary $K_2Cr_2O_7$ to bring it up to strength is weighed out and dissolved in the 900 cc. of remaining solution. Examples—

1. It was found that only 99·6 cc. were required, hence each 99·6 cc. require diluting with 0·4 cc. of water, therefore the 900 cc. left require—

$$\frac{900 \times \cdot 4}{99 \cdot 6} = 3 \cdot 7 \text{ cc. of water adding to them to}$$

make the standard solution correct.

2. On titrating 100·5 cc. of the standard solution were required.

Hence in 900 cc. the error is equivalent to 4·5 cc. of water devoid of bichromate.

Then if 1000 cc. require 1·7813 grammes $K_2Cr_2O_7$

$$4 \cdot 5 \quad ,, \quad x \quad ,, \quad ,,$$

$$\frac{1 \cdot 7813 \times 4 \cdot 5}{1000} = 0 \cdot 008 \text{ gramme } K_2Cr_2O_7$$

Thus 8 milligrammes of bichromate are required to bring the solution to its proper strength, which should, however, be checked by a second titration. In works laboratories it is best to make up and standardize a large Winchester quart (holding several litres) of solution.

The blue colour produced by *ferrous* salts with potassium ferricyanide is due to a precipitate, or, in dilute solutions, to an emulsion of ferrous ferricyanide or Turnbull's blue, which has the empirical formula $Fe_5(CN)_{12}$. *Ferric* salts

give only a very faint brown coloration with dilute solutions of red prussiate of potash. It will be seen that the principle underlying the reactions occurring in the volumetric estimation of manganese is—

1. The measurement of the oxygen taken by the residual ferrous iron from the bichromate.

2. From the above datum the determination of the oxygen originally yielded to the ferrous iron by the manganese dioxide.

In the first-named reaction chromic anhydride CrO_3 is reduced to chromic oxide Cr_2O_3, and the ferrous oxide FeO is oxidized to ferric oxide Fe_2O_3.

In the second reaction, manganese peroxide MnO_2 is reduced to manganous oxide MnO, and the liberated atom of oxygen converts its atomic equivalent of FeO to Fe_2O_3.

The student should thoroughly master these reactions, because they will be again used for several analyses to be described later on. Their mastery necessitates a thorough knowledge of elementary inorganic chemistry, particularly with reference to the displaceable hydrogen of acids, the existence of higher and lower basic oxides, and the formation of both acid-forming and basic oxides by the same metal.

Colorimetric Estimation of Manganese.

(Time occupied, about 2 hours.)

This method bears a general resemblance to that by means of which combined carbon is estimated by colour, and several of the precautions given as absolutely necessary to obtain accurate results for the latter process apply with equal force to the present method. In the first place, a set of standard steels, the manganese present in which

has been settled as the mean of several concordant estimations, is required. The following table shows a useful set of standards, the percentage of manganese in the steels with which the respective standards should be employed, and the most convenient weight of steel to be taken for analysis.

Approximate Manganese % in the standard steel.	per cent. of Manganese in the steel under examination.	Convenient weight in grammes to use for analysis.
0·15	0·1 to 0·2	0·15
0·30	0·2 " 0·4	0·10
0·60	0·4 " 0·8	0·07
1·00	0·8 " 1·2	0·05
1·40	1·2 " 1·6	0·03

In the author's opinion, it is not advisable to attempt to estimate manganese by the colour test much above the limit indicated in the above table.

The Process.

Re-agent required: pure, clean red-lead, $Pb_3O_4 = (PbO)_2PbO_2$.

Weighing out.—Weigh out into clean, dry test tubes, 6 in. long by ½ in. diameter, and marked at 10 cc., equal weights of the steels and their requisite standards, the percentage of the latter and the distinguishing number of the former being attached by means of a little square of gummed paper.

Dissolving.—Add to each tube from a burette 3 cc. of nitric acid, sp. gr. 1·2, and dissolve the steels exactly as for carbons on p. 49.

Diluting.—Next dilute each solution with 3 cc. of water.

Addition of Pb_3O_4.—After well boiling the bath for five minutes, add to each tube about 1 gramme of red-lead, which is conveniently delivered into the solutions from a glass tube. The latter may be made to measure out the proper weight of re-agent in the following manner. Take a glass tube 6 mm. in diameter and about 200 mm. long, and grind its ends level on stretched emery cloth. Then fit into it a glass rod ground quite flat at one end, and having a knob at the other, so that when the bulged-out portion rests on one end of the tube, the flat face of the rod is 9 mm. from the other end. The rod should very closely fit the bore of the tube. Completely and compactly fill the vacant portion with Pb_3O_4 by dipping it into the wide-mouthed bottle holding the re-agent. Withdraw the glass rod (which during the filling requires holding tightly in position), and with another made in exactly the same way, and of the same diameter, but 230 mm. long, cautiously project the moulded and adherent piece of red-lead into the acid.

Boiling.—Next briskly boil the bath for five minutes.

Diluting.—Take out the tubes, and with the wash-bottle jet dilute each solution till the meniscus of the liquid is on the 10 cc. mark.

Mixing.—Well mix the contents of each tube by means of a flat-headed glass rod plunger. The latter, after shaking free from adherent liquid, may be used from solution to solution without perceptible error.

Settling in the dark.—Next place the rack containing the tubes in a dark cupboard, and allow the deep brown PbO_2 to settle for at least an hour, till the liquid is quite clear from suspended oxide.

Comparing the colours.—The purple liquids are then conveyed to 20 cc. stoppered and graduated tubes by

means of a 5 cc. ball pipette of such a size that the ball lodges on top of the test tube, whilst the pointed end of the stem is at least one inch from the bottom; the mark of the pipette should be just above the ball. Withdraw and deliver exactly 5 cc. of each solution into the comparing tubes: the pipette need not be washed, but should be shaken free from visible liquid at each withdrawal. The standard is made up to the mark, the stopper of the tube inserted, and the liquid thoroughly mixed, just as in the carbon test. The solution of the unknown steel is diluted and mixed (always using the stopper and not the finger to close the mouth of the tube), till the colours match when compared against the wet filter-paper, after using the precaution referred to on p. 51, of reversing the relative positions of the tubes before deciding on the final reading. The following table indicates the volume to which the various standards should be diluted, and the conversion of the cc.s registered by the steels under analysis into percentages.

Mn % in standard, say.	Dilute to cc.	To convert cc. registered by Steel into % *Mn*.
0·14	7·0	Multiply by 0·02
0·31	6·2	" " 0·05
0·58	11·6	" " 0·05
1·03	10·3	" " 0·10
1·42	14·2	" " 0·10

Examples.

1. With the 0·14 standard the unknown steel matched at 6·2 cc. $6{\cdot}2 \times {\cdot}02 = 0{\cdot}124$, say 0·12 % *Mn*.

2. With the 0·58 standard the steel registered 10·4 cc. $10{\cdot}4 \times {\cdot}05 = 0{\cdot}52$ % *Mn*.

3. With the 1·42 standard the steel required diluting to 13·7 cc.. $13·7 \times ·1 = 1·37$ % *Mn*.

Theory of the Colour Process.

When the red-lead is added it forms nitrate of lead, and precipitates dark PbO_2, thus—

$$(2\,PbO + PbO_2) + 4\,HNO_3 = 2\,Pb(NO_3)_2 + 2\,H_2O + PbO_2$$

The PbO_2 by a complex reaction oxidizes the manganous nitrate into purple red permanganic acid $HMnO_4$, the colour being within reasonable limits proportional to the manganese present. The solution is gradually bleached by light, hence the advisability of allowing the excess of peroxide of lead to settle in the dark. Permanganic acid is readily reduced (of course losing its colour) by contact with organic matter;[1] for this reason it is safer to make the comparisons in stoppered tubes. The success of this colour process seems to a great extent to depend upon having the manganese present in exceedingly small quantities, together with a fairly large excess of PbO_2.[2] The method is not available for chrome steels.[3] Some chemists prefer to carry out the oxidation in a bath of chloride of calcium solution, which boils at about 110° C. Such a liquid may be obtained by dissolving 500 grammes of the fully hydrated salt ($CaCl_2 + 6\,H_2O$)

[1] The carbon colouring matter seems to be destroyed during the process.

[2] The author has attempted to estimate the manganese in 0·5 gramme of steel, by converting the element by the foregoing process into permanganic acid, and titrating the latter with a dilute solution of ammonium oxalate, but the results were not satisfactory.

[3] These are not completely soluble in nitric acid, and, moreover, the dissolved chromium is converted by the PbO_2 into yellow chromic acid H_2CrO_4.

in 500 cc. of water, but the author has never found its employment attended by any noticeable advantage.

The red-lead used should be ascertained by a blank experiment (made on 3 cc. of 1·20 acid, 3 cc. of water, and 1 gramme of Pb_3O_4) to be quite free from every trace of manganese, otherwise the amount added to each tube must be exactly weighed so as to give a constant error: this procedure, however, should if possible be avoided, as samples of manganese-free red-lead are obtainable.

Comparative values of the three methods given for estimating Manganese.

Gravimetric.—There is no doubt that when time permits the gravimetric process is the best to use, being the most uniformly reliable method, and in disputed cases it should always be appealed to.

Volumetric.—The volumetric process is valuable for rapidly obtaining practically accurate results within a long range of percentage when time presses.

Colorimetric.—The colour test is useful for deciding roughly in about thirty minutes the quantity of manganese present in any given steel, because, with a little experience, this can be done without waiting for the PbO_2 to fully settle, or comparing in the comparison tubes with the standard. It is also of great service in works making each day a considerable number of steel heats of practically constant composition, in all of which the chemist is required to rapidly check the percentage of manganese present. In such cases, a set of standards is not necessary: for instance, in an open-hearth works the manganese is usually kept pretty constant at about 0·5 %. Then, with

a standard approximating this percentage, although in a heat abnormally high or low in manganese the metal might not be accurately estimated, the colour test would nevertheless indicate the composition to be seriously wrong, and the working up or delivery of the steel could be delayed till a gravimetric or volumetric estimation had been made.

The author's experience of the comparative results obtained by skilled operators when working the three processes is, that the volumetric results fall 0·02 % below those obtained by the gravimetric method, whilst the percentages registered by the colour test may fall 0·03 % below or rise 0·03 % above results obtained by the acetate method.

The above statements of course have reference to returns obtained when the respective methods have been worked under the conditions herein laid down.

Gravimetric Estimation of Sulphur.

Re-agent required.

Barium chloride.—A 10 % solution of barium chloride ($BaCl_2$) is made by dissolving 67 grammes of the pure hydrated salt in half a litre of water. Filter if necessary, and store in a stoppered bottle for use.

The Process.

(Time occupied, about $1\frac{1}{4}$ days.)

Weight taken.—Weigh out 6 grammes of the steel into a 20-oz. beaker.

Dissolving.—Put on the cover, and pour down the lip

10 cc. at a time 60 cc. of aqua regia, allowing the violent reaction to subside after each addition. Quietly boil on the plate till the steel is dissolved, and then more briskly, till the solution gives indications of spitting.

Evaporation to dryness.—Move the beaker to a less hot part of the plate, take off the cover, allowing the drops of liquid on it to drain down the inside of the beaker, and place it convex side up on a filter-drier. Cautiously evaporate the liquid to complete dryness, and bake the dry mass of ferric chloride on the hottest part of the plate for at least half-an-hour.

Re-dissolving.—Remove the beaker, holding it in the hand or placing it on a pad of warm asbestos till moderately cool. Replace the cover, and dissolve up the dry mass by boiling it with 40 cc. of strong HCl solution.

Evaporation to low bulk.—Very gently evaporate down till the dark-brown mirror-like liquid measures not more than 10 cc.

Fractional Filtration.—Add 10 cc. of water, and wash the solution without loss into a 60 cc. graduated flask: place the flask in cold water, and when its contents have cooled, dilute to the mark and thoroughly mix. Filter off 50 cc. through a dry 110 mm. pure filter into a graduated flask. Transfer the liquid from the latter into a clean, dry 20-oz. beaker, and well wash out the flask with a little water, of course adding the washings to the main solution.

Precipitation.—Next add 20 cc. of the 10 % solution of $BaCl_2$, when the bulk of the liquid should measure about 100 cc. Well mix the liquid in the beaker by shaking it round, put on the cover, and allow the solution to stand for a night.

Filtration.—In the morning filter off the precipitate

on to a 90 mm. close-grained paper contained in a 2-in. plain funnel with a short stem supported in a 100 cc. measuring-glass. Pass through as much as possible of the clear supernatant liquid without much disturbing the precipitate, and throw away the iron solution after ascertaining it to be free from suspended, finely-divided precipitate. It is probable that when the main quantity of the latter is thrown upon the filter some will pass through into the filtrate, and as long as this happens, the latter must be re-passed through the paper till the pores of the filter are filled up and the liquid passes through quite clear. Every particle of the barium precipitate must of course be washed out of the beaker into the filter.

Washing.—Very carefully wash the edges of the paper alternately with very dilute hot HCl (5 cc. of strong HCl solution to 45 cc. water) and cold water till quite free from iron salts, when a few drops of the washings added to a dilute solution of ammonium sulphocyanide will develop no pink tinge.

Drying.—Dry the precipitate as usual on the hot plate by removing it from the funnel and supporting it in an earthenware cylinder.

Igniting and weighing.—Fold the paper and ignite in the muffle in a clean, tared 2-in. porcelain crucible till quite white. When thoroughly cold, remove the crucible from the desiccator and re-weigh. The increase is sulphate of barium $BaSO_4$, containing 13·7 % of sulphur. The result is of course calculated on 5 grammes of steel.

Blank estimation of sulphur in re-agents.—It is frequently necessary, in order to ensure accurate results, that a blank estimation of the sulphur existing in the re-agents used be made, and the weight of $BaSO_4$ thus obtained be deducted

from the apparent weight of $BaSO_4$ derived from the steel. In order to save time, the best plan is to set aside a Winchester quart each of aqua regia and hydrochloric acid, and in these determine, once and for all, as the mean of a duplicate estimation, the weight of $BaSO_4$ resulting from the exact volume of these acids employed in an estimation of the sulphur in the steel. This is best done by going through the analysis exactly as in an actual determination, except that a pinch of pure Swedish bar iron (which contains only about 0·01 % of sulphur) is used to fix the sulphur which exists in the re-agents as free H_2SO_4 as non-volatile sulphate of iron.

Without this precaution, the sulphuric acid would be driven off on evaporating the original solution to dryness, and the result might indicate really impure acids to be sulphur-free. Perfectly sulphur-free acids are somewhat rare, and the manufacturer's assurance on this point must never be taken for granted.

Model of Record and Calculation.

June 30, 1889. Drillings from steel rail. Blow 740.

Weight taken 6 grammes.

$$
\begin{array}{rr}
\text{Crucible + ppt. + ash} = & 25{\cdot}6192 \\
\text{Weight of crucible} = & \underline{25{\cdot}5727} \\
 & {\cdot}0465 \\
-\text{(Blank + ash)} = & \underline{{\cdot}0072} \\
BaSO_4 = & {\cdot}0393 \\
 & \underline{13{\cdot}7} \\
 & 2751 \\
 & 1179 \\
 & \underline{393} \\
 & 5)\,{\cdot}53841 \\
 & \underline{\underline{0{\cdot}108\ \%\ S}}
\end{array}
$$

Theory of the Aqua Regia Process.

On dissolving the steel, the nitro-hydrochloric acid oxidizes the sulphide of iron present to ferric sulphate; the silica is rendered insoluble by the evaporation to dryness, and is separated by the fractional filtration, which dispenses with the necessity of washing the filter-paper. On adding the solution of barium chloride to the slightly hydrochloric acid solution of the ferric sulphate, insoluble barium sulphate is precipitated thus—

$$Fe_2(SO_4)_3 + 3\ BaCl_2 = 2\ FeCl_3 + 3\ BaSO_4$$

It was formerly deemed necessary, in order to ensure accurate results, to evaporate the solution of ferric chloride till a scum began to form upon its surface, thus getting a liquid containing practically no free hydrochloric acid. It was also the rule to precipitate the $BaSO_4$ from a largely-diluted solution. The necessity for these precautions, like many other chemical traditions, had no foundation in fact. Mr. L. Archbutt, in a very useful investigation on this point, proved that better results are obtained in a fairly concentrated solution containing a moderate excess of free acid, than under the old conditions. Subsequent trials by the author fully confirmed the accuracy of Mr. Archbutt's main conclusion, but his plan of precipitating the $BaSO_4$ from a rather concentrated solution of ferric chloride at a boiling heat is, in the author's opinion, inadvisable, the ignited precipitate under these conditions being frequently red with a small quantity of oxide of iron, due to the precipitation with the barium sulphate of obstinately retained basic iron salt, insoluble in very dilute hydrochloric acid.

Gravimetric Determination of Sulphur by the Evolution Method (Fresenius, modified).

On referring to the reactions of hydrochloric acid upon steel (page 57), it will be seen that the sulphide of iron existing diffused throughout the mass of the steel, is totally decomposed by the acid with evolution of H_2S gas. Many methods have from time to time been proposed, having for their object the oxidation of the evolved sulphuretted hydrogen to sulphuric acid, so that the latter on precipitation as $BaSO_4$ should become the measure of the sulphur in the steel. The best method of this type is that in which the H_2S is oxidized by bromine; for this purpose, the author has devised the modification about to be described.

Apparatus required.

Fill up the arrangement sketched in Fig. 13: A is a glass gas-holder filled with hydrogen, previously washed through strong caustic soda solution;[1] B is a full-necked 12-oz. flask, carrying in its india-rubber stopper an inlet tube for the hydrogen, a 50 cc. stoppered separator, and an outlet bend for the gases evolved from the steel; the rack C is, however, replaced by the absorption cylinder X of about 150 cc. capacity, 30 mm. internal diameter, marked at 20 and 120 cc., and having below the first-named mark

[1] Prepare the hydrogen from dilute hydrochloric acid and granulated zinc placed in a filter pump vessel, with a side leading tube. The flask is fitted with an india-rubber bung carrying a 50 cc. stoppered separator from which to deliver the acid. The strong *NaHo* solution is contained in a washing cylinder fitted with an india-rubber bung with two holes carrying the usual bent tubes.

a glass tap (Fig. 12). The top of the parallel cylinder is ground inside, and provided with a well-fitting glass

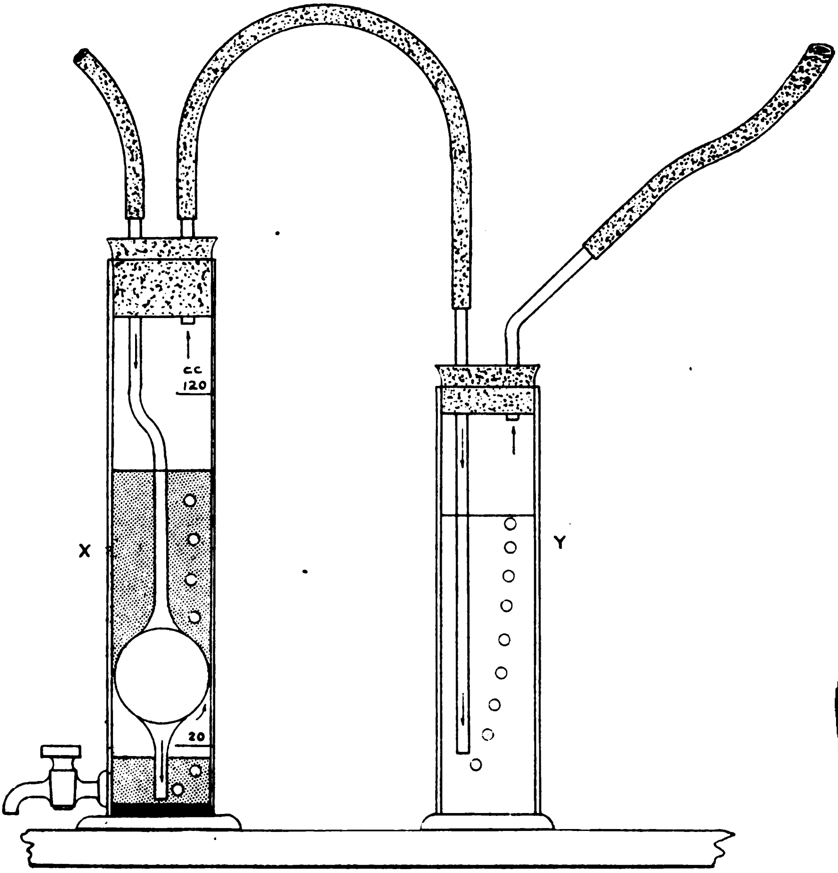


FIG. 12.

stopper. During the absorption, however, it is closed with an india-rubber stopper carrying a curved inlet tube (on

which has been blown a bulb 0·2 mm., smaller than the inside diameter of the cylinder), and an outlet bend. Y (Fig. 12) is a washing cylinder containing strong caustic soda solution, and it is attached between X (Fig. 12) and aspirator D (Fig. 13). The parts of the apparatus are connected together with good thick-walled india-rubber tubing, and the india-rubber stopper in the absorption cylinder must have been freed from surface sulphur by boiling with dilute caustic soda, and afterwards in several changes of water.

The Process.

(Time occupied, about 4 hours.)

Weight taken.—Weigh out into the 10-oz. flask 6 grammes of the steel in drillings.

Removing the air.—Cover the drillings with about 30 cc. of recently-boiled water (under which the hydrogen inlet tube must dip), and set up the apparatus, having previously charged the absorption cylinder with 3 cc. of pure bromine and 90 cc. of a saturated solution of bromine water. Having seen that the system is air-tight by opening the aspirator tap (when the passage of air through the cylinders should soon cease), gently open the hydrogen tap, and pass about half a litre of the gas through the apparatus.

Dissolving.—Shut off the hydrogen, and run in from a separator about 50 cc. of strong HCl, and close the tap without quite emptying the bulb. The steel may at first be left to dissolve in the cold, being afterwards assisted to complete dissolution by gently heating the sand-bath, and finally bringing the clear acid solution just to boiling. Then remove the lamp, quietly aspirate about half a litre

of hydrogen through the apparatus to carry forward every trace of H_2S into the bromine tube; then close the aspirator tap, and force through the hydrogen till the equilibrium inside the apparatus is restored.

Precipitation of the SO_3.—Detach the bromine tube from the flask and the washing cylinder. Remove and rinse the bulb tube inside and out, and dilute the contents of the cylinder with distilled water to the 120 cc. mark. Put in the glass stopper, and well mix the liquid by inverting two or three times. Take out the stopper, and tap off into a clean 20-oz. beaker 100 cc. of the brown solution containing the sulphur in 5 grammes of steel. Cover the beaker, and bring its contents to boiling on a plate in the draught cupboard till the bromine is driven off; then add down the lip 5 cc. of pure strong HCl solution and 20 cc. of the 10 % solution of barium chloride. Boil for 15 minutes, to render the precipitated $BaSO_4$ crystalline, in which condition it is less liable to pass through the pores of the filter-paper.

Treatment of the precipitate.—The barium sulphate may be at once filtered off: it is washed, dried, ignited, and weighed exactly in the manner already described for the estimation of sulphur by the aqua regia method on page 98, only, as the liquid from which the $BaSO_4$ was precipitated was free from iron salts, the filter will not require washing with dilute hydrochloric acid, but with hot water only.

Theoretical Considerations.

The reason for using recently-boiled water for covering the drillings is, that during the preliminary hydrogen aspiration, they are liable to become somewhat rusted by

the action of the dissolved oxygen in ordinary water, from which the oxygen is expelled on boiling. The rust or Fe_2O_3 would form $FeCl_3$ on the addition of HCl, and the ferric chloride might possibly decompose, and thus prevent the evolution of a small volume of H_2S by the reaction given on p. 183. A similar reason exists for sweeping out the air, the oxygen of which converts a little of the H_2S into sulphuric acid, which remains in the flask.

The action of the bromine on the evolved H_2S gas is formulated in the following equation—

$$H_2S + 8\ Br + 4\ H_2O = 8\ HBr + H_2SO_4$$

Sulphuretted hydrogen, bromine, and water yield a mixture of hydrobromic and sulphuric acids: the bromine used must of course be sulphur-free, and in setting up any modification of the foregoing installation, it must always be borne in mind that india-rubber stoppers and tubing contain sulphur oxidizable by bromine, and if carelessly arranged may lead to mysteriously high results. The cylinder of sodic hydrate solution serves to absorb the bromine vapour carried away with the gases, which, if allowed to escape into the air of the laboratory, would prove exceedingly irritating to the eyes and lungs. The reaction of the absorption is—

$$2\ NaHO + 2\ Br = NaBr + NaBrO + H_2O$$

Sodic hydrate and bromine yield sodium bromide, sodium hypobromite, and water. It will be noticed that the bromine absorption tube is constructed on the principle already described on p. 38 for potash bulbs.

Volumetric Estimation of Sulphur

(Author and Hardy).[1]

Re-agent required.

Standard solution of lead acetate.—Pick out from the centre of larger crystals of pure acetate of lead [$Pb(C_2H_3O_2)_2$, $3\ H_2O$] small bright fragments of the fully hydrated salt, and weigh out into a litre flask 1·182 grammes, dissolve in 100 cc. of distilled water and 10 cc. of P.B. acetic acid, then with distilled water make up the liquid to exactly 1000 cc., and thoroughly mix the solution to ensure equal diffusion of the lead salt. Preserve the standard fluid in a well-stoppered bottle, labelled, "$Pb(C_2H_3O_2)_2$. 2 cc. = 0·01 % S in two grammes of steel."

The Process.

(Time occupied, about $1\frac{1}{4}$ hours.)

Weight taken.—Weigh out into an 8-oz. full-necked dry flask 2 grammes of drillings, and cover them with 30 cc. of recently-boiled distilled water.

The apparatus.—Attach the flask to the apparatus sketched in Fig. 13. A is a glass gas-holder containing hydrogen washed through a strong solution of caustic soda; B is the flask carrying an india-rubber stopper in which is an inlet tube (dipping under the surface of the water), a 50 cc. stoppered separator, and an exit bend for the gases; C is a rack containing from three to thirteen tubes (according to the nature of the material under analysis), each previously charged with 2 cc. of the

[1] *Chemical News*, 1888, No. 1496.

standard lead solution accurately delivered from a burette. A full-sized sketch of a pair of the bulb tubes is given in Fig. 14. They work upon the principle of the potash bulb described on p. 38. The first tube in the rack is not charged with standard solution, but with 1 cc. of distilled water: it acts as a condenser for fumes of *HCl*. D is a glass aspirator, graduated in half litres. Throughout, the apparatus should be provided with well-fitting india-rubber stoppers, and the connections must be of sound thick-walled india-rubber tubing.

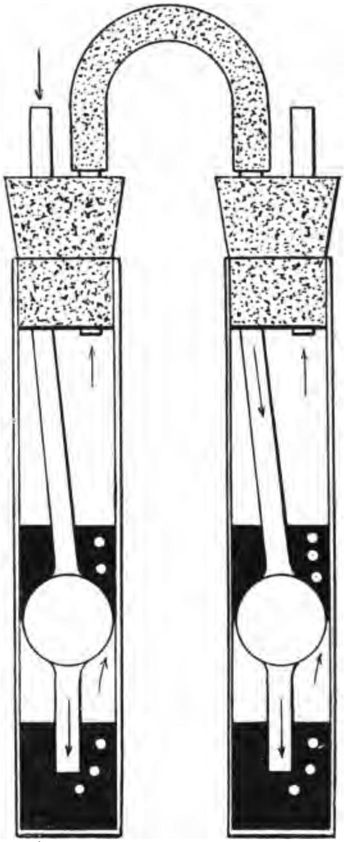


FIG. 14.

Displacing the air.—Having tested the tightness of the apparatus by opening the aspirator tap, and noting that the flow of air soon ceases, very gently open the gas-holder tap, and sweep out the air by aspirating at least half a litre of hydrogen through the system.

Dissolving the steel.—Close the hydrogen tap, and put in the separator 35 cc. of strong hydrochloric acid solution, run in about 30 cc., and close the tap. For the first few minutes the evolu-

tion may be allowed to proceed in the cold, but when the flow of gas slackens, a gentle heat is applied to the sand-bath supporting the flask till the steel is completely dissolved, when the liquid is just brought to boiling; the Bunsen is then removed. During the whole operation the flow of gas should be kept regular and somewhat slow; as it proceeds tube after tube will blacken from the formation of PbS, which is at first in an emulsified condition, but afterwards precipitates in flocks in the first one or two tubes. As the solution reaches boiling-point, open the hydrogen tap, and carry forward the last traces of H_2S into the registering tubes by aspirating about half a litre of the gas. Then read off the percentage. Each tube blackened equals 0·01 % S. There is no difficulty in reading to 0·005 % represented by the last tube, being evidently only partially saturated with sulphur at the end of the process.

Cleaning the tubes and bulbs.—These are readily cleared from adhering PbS by respectively filling and dipping them with and into warm dilute nitric acid, after which they must be very thoroughly washed with water before being again used, otherwise the next estimation will be worthless, owing to the oxidation of the dark PbS to colourless $PbSO_4$ by any traces of nitric acid present.

Theoretical Considerations.

The principle of the evolution method has been already described in the article on the bromine process. The reaction between the lead acetate and the evolved H_2S is—

$$Pb(C_2H_3O_2)_2 + H_2S = PbS + 2\ C_2H_4O_2$$

Lead acetate and hydrogen sulphide yield dark-brown sulphide of lead and free acetic acid. By the above equation it will be seen (remembering that the original lead salt contained three molecules of water) that 378 parts by weight of the acetate combine with 31·98 parts of sulphur. The standard solution was made by dissolving 1·182 grammes of acetate in 1000 cc. of water.

Therefore $\frac{1 \cdot 182}{1000} = 0 \cdot 001182$ parts of acetate combine with—

$$\frac{31 \cdot 98 \times 0 \cdot 001182}{378} = 0 \cdot 0001 \text{ parts of } S.$$

or 1 cc. = 0·005 % S in 2 grammes of steel.
∴ 2 cc. = 0·010 % S " " "

The remarkable absorptive power of the bulbs enables them to sharply separate each increment of one-hundredth %, no H_2S reaching a bulb till the lead in its fellow next the evolution flask has fixed its equivalent of sulphur; but the proportions of the bulbs and cylinders must be accurate, so that the liquid is always divided into two layers during the passage of gas, one above and the other below the bulb. If the latter is too small the liquid will remain unbroken, if it is too large, nearly the whole of the solution will be driven to the top of the bulb, leaving a small layer of liquid through which the gases do not bubble at the bottom of the inlet tube: the dimensions should be strictly in accordance with the full-sized sketch. The phosphoretted hydrogen evolved from the steel has no action upon the lead salt, and the current of hydrogen aspirated at the end of the dissolution carries forward from the saturated tubes the H_2S present merely in aqueous solution till it is fixed by its equivalent of lead in the next unsaturated tube. It is an interesting fact, that the evolution of sulphur during the process is not proportional to the steel dissolved, because when only

about half the steel has passed into solution, about two-thirds of the total sulphur has been evolved.

It is of great importance that the acid used be devoid of *free* chlorine, which would oxidize the H_2S to H_2SO_4, in which form it would remain in the flask, and its registration in the lead tubes would be missed. The acid should be tested with starch and pure KI in the manner described on p. 175, the hydrochloric being substituted for the acetic acid.

After five years' experience of the working of this process in carrying out many hundreds of estimations (occasionally checked by precipitating the sulphur as $BaSO_4$), the author has no hesitation, as far as the cases of completely soluble steels and bar-irons are concerned, in pronouncing it to be a most accurate and rapid method. The process, however, in the case of grey hematite pig-irons containing about 0·05 % of sulphur has not worked so satisfactorily, results as much as 0·02 % low having been occasionally registered; but with Spiegel and Swedish white iron good results have been obtained.

THE GRAVIMETRIC ESTIMATION OF PHOSPHORUS IN STEEL.

There are several accurate gravimetric methods by means of which phosphorus may be determined in steel. First, the molybdate process (Eggertz); second, the magnesia process; third, the combined molybdate and magnesia process.

The process first mentioned may be carried out in two ways, which will herein be designated as the rapid and the long methods.

The Rapid Process (Stead and Cook).

(Time occupied, about 2 hours).

Re-agent required.

A 10 % solution of ammonium molybdate.—This is prepared by dissolving 50 grammes of the pure, absolutely phosphorus-free salt in about 400 cc. of hot water. The solution when cold is diluted to 500 cc., is filtered, and preserved for use in a stoppered bottle.

The Method.

Weight taken.—Weigh out two grammes of the *perfectly clean* steel drillings into a 20-oz. beaker.

Dissolving.—Pour down the lip of the covered beaker 30 cc. of nitric acid, sp. gr. 1·2. When the first violent reaction has subsided, heat the liquid on the plate till the steel has dissolved, then add 7 cc. of strong *HCl* solution, and boil the liquid for a few minutes.

Precipitation with ammonia.—Remove the beaker from the plate, rinse the cover and sides of the beaker, and replace the former. Allow the liquid to stand until moderately cool. Pour down the lip of the beaker, little by little, dilute ammonia (half 880, half water), well shaking round the beaker after each addition of alkali till the acids are neutralized, the iron completely precipitated as hydrate, and an excess of 4 or 5 cc. of the ammoniacal liquid has been added. The beaker must be well shaken round, till the mass forms a fluid paste smelling strongly of ammonia.

Re-dissolving the iron.—Pour down the lip of the beaker from a 10 cc. measuring-glass strong nitric acid, 1 cc. at a

time (well shaking round after each addition), till the iron precipitate has completely dissolved. Then add 3 cc. more of the strong nitric acid. Boil down the liquid till it measures about 40 cc., and any splashings of hydrate of iron formed during the treatment with ammonia have dissolved off the cover and sides of the beaker.

Precipitating the phosphorus.—Remove the beaker from the plate, take off and rinse the cover, and by means of a pipette, deliver into the centre of the hot liquid 15 cc. of the 10 % solution of ammonium molybdate. Gently shake the liquid round, till any pale yellow flocks of precipitated hydrate of molybdenum have dissolved. Next digest the contents of the beaker on a comparatively cool corner of the plate or on the top of the air-bath (occasionally well shaking it round) for fifteen or twenty minutes, till the yellow precipitate readily settles to the bottom of the beaker on standing a little after the last shaking.

Filtering.—Collect the precipitate on a 90 mm. hardened filter-paper, contained in a 2-in. funnel. Rinse out the beaker (the aid of a policeman should not be required) with a fine jet of water containing about 2 % of strong nitric acid. Wash the paper, and precipitate three or four times till free from any visible traces of iron solution, and allow the filter to drain.

Drying the precipitate.—Cautiously spread out the filter-paper on the convex side of a 5-in. clock-glass, so that the edge of the paper nearest the precipitate projects over the edge of the glass. Then, by means of a very fine jet of cold water, wash the precipitate into a clean, tared platinum or porcelain dish about 2½ in. diameter. With a sufficiently fine wash-bottle jet 20 cc. of water should suffice for this purpose. Place the dish on the hot plate over a little beaker of boiling water, and evaporate its

contents to dryness. Remove the dish, and dry it outside with a clean duster, and place for five minutes in the air-bath at 100° C.

Weighing.—Allow to cool in a desiccator, and, as quickly as possible, the yellow precipitate being hygroscopic, re-weigh the dish; the increase is ammonio-phospho-molybdate, containing 1·63 % of phosphorus.

Example of Calculation.

May 6, 1880. Bessemer Rail. Blow 932.

Weight taken 2 grammes.

Dish + precipitate	=	32·6394
Weight of dish	=	32·5482
		·0912
		1·63
		2736
		5472
		912
		2)·148656
		0·074 % P

Theoretical Considerations.

The foregoing modification of the molybdate process is essentially that devised by Messrs. Stead and Cook for the determination of phosphorus in basic steels practically free from silicon, it being a canon of analytical faith, that silicic acid was carried down from its nitric acid solution with the molybdic precipitate. This, however, as far as ordinary steels are concerned, was a groundless fear, as the author has proved that even with steels containing 0·2 % of silicon, practically the whole of the silica is found in the

filtrate on evaporating the latter twice to dryness with strong hydrochloric acid. This fact extends the applicability of the process, which, however, should only be employed within the following limits:—

(*a*) For steels containing 0·04 % and upwards of phosphorus.

(*b*) For steels absolutely free from any insoluble residue, such as tungsten, scale, etc.

(*c*) For steels containing under 1 % of combined carbon, because an excessive amount of organic colouring matter has a tendency to prevent the complete precipitation of the phosphorus.

The author, to ensure the complete original solution of the silicon, has slightly modified the directions given by Messrs. Stead and Cook for dissolving the steel. Irrespective of this point, he has never been able to follow the published instructions, namely, to "dissolve two grammes of the steel in 12 cc. of nitric acid, sp. gr. 1·42, and 5 cc. of water," simply because two grammes of steel will not completely dissolve in such a mixture.

The foregoing method is rapid, and when carried out with care, gives concordant and accurate results; but slight violations of the empirical conditions necessary for success may cause the process to register percentages in some cases seriously below, in others considerably higher, than the true phosphorus. The conditions under which the yellow precipitate is formed are not well understood. It was formerly supposed that chlorides should be absent, but it is now generally admitted that, excepting hydrogen chloride, they even favour the precipitation, if coincident with the other absolutely necessary conditions, which are specified below.

1. The iron must be in nitric acid solution, with free

acid in some excess. If, however, the excess is too great, the result is low, or in extreme cases no precipitate is obtained. If insufficient free nitric acid is in the liquid, the latter is dark in colour, and the precipitate thrown down has a reddish tinge, due to the presence of basic nitrate of iron carried down with it.

2. The presence of a large amount of ammonium nitrate is necessary.

3. The presence of a large excess of ammonium molybdate, say 500 times the weight of the phosphorus present, is very important.

4. The temperature of the precipitation must be kept well under 100° C., or free molybdic acid may be precipitated, causing a high result. A prolonged digestion may also produce the same effect.

5. The total bulk of liquid in which the phosphorus is precipitated should measure from 50 to 60 cc.

It will be seen on comparing the above with the practical directions that the necessary conditions are there secured; but the student should carefully make some experiments on a series of weighings from one steel, trying to get accurate results, high results, or low results by respectively adhering to or suitably violating the conditions given. He will thus learn how to estimate "phosphorus by molybdate" with a far more enduring knowledge than written instructions can convey.

Mr. A. A. Blair precipitates phosphorus by adding a nitric acid solution of ammonium molybdate and nitrate to a solution of ferric chloride and phosphate containing some free hydrochloric acid. Results obtained under such conditions are invariably seriously low. The reactions taking place during the determination of phosphorus by the rapid molybdate process are as follow :—

1. The phosphide of iron present in the steel is oxidized by the nitric acid to phosphate (see p. 60), and the silicon forms a stable solution of silicic acid (see p. 60).

2. The neutralization of the free nitric and hydrochloric acids by ammonia with formation respectively of ammonium nitrate and chloride, takes place thus:

$$HNO_3 + AmHO = AmNO_3 + H_2O$$
$$HCl + AmHO = AmCl + H_2O$$

3. The complete precipitation of the iron as hydrate (and to the extent of the phosphoric acid present as phosphate) by the excess of ammonia, occurs thus—

$$Fe(NO_3)_3 + 3\ AmHO = Fe(HO)_3 + 3\ AmNO_3$$

4. The neutralization of the excess of ammonia and the re-solution of the precipitated hydrate (and phosphate) of iron by excess of nitric acid, takes place thus—

$$Fe(HO)_3 + 3\ HNO_3 = Fe(NO_3)_3 + 3\ H_2O$$

5. The precipitation of ammonio-phospho molybdate by the addition of excess of ammonio molybdate, is effected thus—

$$FePO_4 + 11\ Am_2MoO_4 + 22\ HNO_3 = \underbrace{[Am_3PO_4,\ 11\ (MoO_3\ 6\ H_2O)]}_{\text{(The yellow precipitate)}} + Fe(NO_3)_3 + 19\ AmNO_3 + 11\ H_2O$$

The yellow compound containing the phosphorus cannot be ignited in the ordinary way, because when strongly heated it decomposes, leaving a fixed residue of dubious composition.

On drying at 100° C. it loses water, leaving a residue with the composition (Am_3Po_4, 11 MoO_3, 9 H_2O), which very nearly (but not absolutely) coincides with the 1·63 % of phosphorus which universal practice has indicated to be present.

Other Methods for Estimating Phosphorus.

Re-agent required.

Standard solution of ferric iron.—This is prepared by dissolving in a 20-oz. beaker 2·505 grammes of pure Swedish Lancashire hearth bar-iron in 35 cc. of strong HCl solution, and then adding 3 cc. of strong nitric acid to peroxidize the iron. The solution is boiled down, and finally very gently evaporated, till crystals of ferric chloride begin to separate. These are re-dissolved in cold water, the iron solution is transferred without loss to a 250 cc. graduated flask, diluted to the mark, thoroughly mixed, and is stored for use in a stoppered bottle labelled "Standard $FeCl_3$ Solution, 1 cc. = 0·01 gramme Fe."

The three processes already mentioned, namely, the magnesia, the long molybdate, and the combined methods, have in common up to a certain point a series of identical operations which will be next described. They may all be employed in cases for which the rapid molybdate method is not suitable, namely, for high carbon steels, and for bar-iron, blister, and cast steels of Swedish origin, which usually do not contain more than 0·02 % of phosphorus. The combined method is perhaps the most strictly accurate, and in the author's experience has yielded slightly higher results than any of the others.

The Preliminary Process.

Weight taken.—Weigh out into a 20-oz. covered beaker 5 grammes of the steel.[1]

[1] Or decide on the weight to be taken for analysis after reference to the table on p. 190.

Dissolving.—Add down the lip of the beaker 50 cc. of nitric acid, sp. gr. 1·2. This should be added 10 cc. at a time, allowing the violent reaction to subside between each addition. Then quietly boil the contents of the beaker till the drillings have dissolved.

Evaporating to dryness.—The solution is then evaporated to complete dryness. The rapidity with which this is accomplished depends to a considerable extent upon the skill of the operator. Any attempt to boil or even to evaporate quickly to dryness without careful attention will entail the loss of the estimation, as the result of a violent spitting of the iron solution. The best plan is to boil down briskly in the centre of the plate till symptoms of spitting develop, and then to alter the position of the beaker so as to bring one side on the portion of the plate just over the edge of the Bunsen flame. The solution on the warmer side of the beaker will then gradually become dry, and the gentle boiling may be continued till there is danger of the drops falling from the cover breaking the hot beaker. At this stage it must be placed on a pipe-stem triangle, and after removing the cover the liquid is carefully evaporated to complete dryness, the dry mass being exposed to a strong final heating in the centre of the plate.

Re-dissolving.—The hot beaker having been allowed to cool in the hand or on a warm asbestos pad, the cover is replaced, and the oxide of iron is dissolved by boiling it with 50 cc. of strong hydrochloric acid.

Reducing the iron.—Transfer the ferric chloride solution without loss to a 30-oz. registered flask, and dilute with hot water to 200 cc. Next add, little by little, constantly shaking round the flask, dilute ammonia (half 880, half water), till the acid is neutralized and a slight permanent

precipitate is obtained; then add, so as to rinse down the sides of the flask, about 100 cc. of strong sulphurous acid solution.[1] The liquid is then well boiled, again neutralized as before with dilute ammonia, 20 cc. of sulphurous acid are added, and the liquid is again briskly boiled till the solution is pale-green in colour, and the smell of SO_2 has disappeared.

Precipitating the $FePO_4$.—Add to the ferrous solution from a pipette 5 cc. of the standard iron solution; shake the liquid well round and bring it to boiling, and gradually add 25 cc. of hot ammonium acetate solution, after which continue the boiling for a few minutes.

Filtering.—Remove the flask from the plate, and allow the precipitate to settle somewhat. It is then collected on a 110 mm. paper, using either the filter-pump or attaching to a 2¼-in. ribbed funnel the filtering loop sketched in Fig. 2. The hot flask should be held in a thick duster, and as much as possible of the clear liquid should be got through before disturbing the precipitate. The at first clear, greenish filtrate soon becomes yellow and turbid, and an apparently large amount of a flaky scum of basic ferric acetate is formed on the surface of the liquid and the sides of the flask. Allow the flask to drain thoroughly into the filter, but do not attempt any washing beyond removing the drop of liquid from the lip of the flask; the filter also is allowed to drain well, and the loop is removed.

Dissolving up the precipitate.—Hang the funnel inside a clean 20-oz. beaker, and boil 30 cc. of strong hydrochloric acid in the flask in which the precipitation took place, till the precipitated scum has passed into solution. Then cautiously drop the hot yellow liquid round the edges of the

[1] Made by saturating distilled water with SO_2 evolved from a syphon of the liquefied gas.

filter-paper till the precipitate is dissolved up; well rinse the flask out into the filter, and wash the latter with hot dilute hydrochloric acid and cold water till free from any yellow tinge, using, however, as little wash liquid as possible.

Evaporating to low bulk.—Remove the funnel and hanger, cover the beaker, and briskly boil down the solution to low bulk, finally gently evaporating with the cover off to about 5 cc.

The yellow liquid thus obtained is next further dealt with in a manner dependent upon which process is to be employed for the final precipitation of the phosphorus. The case of each method will be presently considered.

Theoretical Considerations.

The preliminary solution in nitric acid converts the iron into ferric nitrate, and oxidizes the phosphide of iron to ferric phosphate (see p. 59). On strongly baking the dry mass of ferric nitrate, it is to a great extent denitrated, leaving ferric oxide Fe_2O_3 mixed with highly basic nitrate; the carbonaceous colouring matter is also decomposed. The highly acid ferric chloride solution requires neutralizing before reduction, because the presence of a large amount of free acid prevents the perfect de-chlorinization of the ferric to ferrous chloride. The result would be a bulky precipitate difficult to deal with during the filtration, which, however, could only be obtained by the addition of a very large volume of ammonium acetate. The action of the sulphurous acid on the nearly neutral solution of ferric chloride is as follows:—

$$2\,FeCl_3 + H_2SO_3 + H_2O = 2\,FeCl_2 + H_2SO_4 + 2\,HCl$$ [1]

[1] The second neutralization is necessary to remove the free hydrochloric and sulphuric acids liberated on the first addition of SO_2.

Ferric chloride, sulphurous acid, and water yield ferric chloride, sulphuric and hydrochloric acids. The addition of 0·05 gramme of ferric iron is to ensure the presence of sufficient ferric salt to precipitate the whole of the phosphorus present as ferric phosphate which is insoluble in an acetic acid solution of ammonium acetate. The 5 cc. added are amply sufficient to precipitate 0·15 % P in 5 grammes of steel.

The traces of free mineral acids liberated by the second addition of sulphurous acid [1] are neutralized, and acetic acid is substituted in their place by the decomposition of the ammonium acetate with the formation respectively of ammonium sulphate and chloride, thus—

$$H_2SO_4 + 2\,Am(C_2H_3O_2) = Am_2SO_4 + 2\,C_2H_4O_2$$
$$HCl + Am(C_2H_3O_2) = AmCl + C_2H_4O_2$$

The phosphate of iron mixed with some basic acetate is then precipitated. On dissolving up the unwholesome-looking mixture, the whole of the phosphorus which was contained in the 5 grammes of steel is concentrated into a solution, in which is associated with it only a comparatively small portion of the iron in which it was originally distributed, and the removal of the bulk of the iron in the form of soluble ferrous acetate much facilitates and renders more accurate the subsequent precipitation of the minute percentage of phosphorus present.

[1] The amount of free sulphuric and hydrochloric acids liberated on the first addition of H_2SO_3 amounts to many grammes, thus preventing a complete reduction. Hence the necessity for a second neutralization.

Magnesia Process.

Re-agent required.

Magnesia mixture.—Dissolve 25 grammes of pure magnesium chloride and 25 grammes of pure ammonium chloride in hot water; cool the solution, make up the volume to 200 cc., and add 50 cc. of 880 ammonia solution. Allow the mixture to stand for a day or two, and filter off the clear liquid into a green glass-stoppered bottle provided with an india-rubber stopper.

The Method.

(Time occupied, about 2 days.[1])

Converting the iron into citrate.—Rinse the sides and cover of the beaker containing the 5 cc. of yellow liquid (obtained at the end of the common preliminary operations), and add 15 grammes of pure citric acid, and adding a little water to bring the crystals into complete solution.

Precipitating.—Next add dilute ammonia till the liquid is strongly alkaline, and finally 2 cc. of magnesia mixture. Shake the contents of the beaker well round, cover the latter, and allow it to stand for about twenty-four hours. The total volume of liquid should not exceed 50 cc.

Filtering.—Collect the crystalline precipitate on a 90 mm. filter, carefully detaching every particle adhering to the sides of the beaker with a policeman, and very thoroughly wash the paper with water strongly alkaline with ammonia (1 volume of 880 to 3 volumes of water).

Weighing.—The precipitate is dried, ignited in the muffle in a tared platinum crucible, and weighed with the

[1] Including the preliminary operations.

usual precaution. Its formula is $Mg_2P_2O_7$ (magnesium pyrophosphate), containing 27·93 % of phosphorus. It should be quite white.

Theoretical Considerations.

The citric acid prevents the precipitation of the iron on the subsequent addition of ammonia by forming a soluble double citrate of iron and ammonium—

$$[FeAm_3\,(C_6H_5O_7)]$$

The phosphorus is precipitated as a double phosphate of ammonium and magnesium ($AmMgPO_4$) + Aqua. This compound on ignition loses water and ammonia, thus—

$$2\,NH_4MgPO_4 = Mg_2P_2O_7 + H_2O + 2\,NH_3$$

The foregoing process has been included on account of its chemical interest, but its employment in steel works laboratories has been abandoned by general consent because of the long period necessary for the complete precipitation of the phosphorus.

The Long Molybdate Method (Riley).

Re-agent required.

Nitric acid solution of ammonium molybdate and nitrate.—Dissolve in a 60-oz. beaker 50 grammes of pure molybdic acid (MoO_3) in 200 cc. of dilute ammonia (80 cc. of 880 and 120 cc. of water). Then add without hesitation in one quick pouring 750 cc. of nitric acid, sp. gr. 1·2. Heat the liquid at about 70° C. for an hour or two, allow it to stand for a day, and filter off the clear liquid for use. In the bottle in which it is preserved, yellow

molybdic acid separates after a time, and care must then be taken that none of this precipitate is suspended in the solution when the latter is poured out for precipitating phosphorus; the liquid must, if necessary, be re-filtered before using.

The Process.

(Time occupied, about 1 day.[1])

Obtaining the iron in nitric acid solution.—To the 5 cc. of liquid in hydrochloric acid solution obtained at the end of the common operation, add dilute ammonia till the hydrochloric acid is neutralized, the iron precipitated, and a distinct excess of ammonia is present after thoroughly shaking round the contents of the beaker. Then add, drop by drop, strong nitric acid, till the precipitate is just re-dissolved, being careful to bring into solution any particles adhering to the sides of the beaker as the result of shaking. Bring the liquid to boiling and remove from the plate.

Precipitating the phosphorus.—Add to the hot solution down the lip of the beaker 30 cc. of the clear nitric acid solution of ammonium molybdate; well shake round the liquid, the volume of which should be about 50 cc.

Estimating the phosphorus.—The contents of the beaker are digested, the precipitate filtered off, washed, dried, and weighed, precisely in the manner described for the rapid molybdate process on page 112, in which article also the theoretical considerations have been fully dealt with.

[1] Including the preliminary operations.

The Combined Method.[1]

(Time occupied, about 1¼ days.[2])

In this process the yellow phosphorus precipitate obtained in the last method is well digested at a temperature of about 100°, which ensures the precipitation of every trace of phosphorus, and is admissible because the co-precipitation of some free molybdic acid is a matter of comparative indifference. The precipitate is filtered off, and it and the filter-paper are washed till free from iron with the 2 % solution of nitric acid.

Dissolving the molybdate precipitate.—The funnel is hung inside a small beaker, and the precipitate is dissolved in the smallest possible quantity of hot dilute ammonia, after which the paper is well washed with a fine jet of hot water.

Precipitating the phosphorus.—To the strongly ammoniacal fluid add 2 cc. of strong hydrochloric acid (to form *AmCl*), and shake the liquid round to re-dissolve any precipitated molybdic acid in the excess of ammonia. At this point the volume of the liquid should be made up with strong ammonia to 48 cc. registered by a diamond scratch or slip of paper previously placed upon the beaker. Next, holding the beaker in the right hand, and continuously rotating its contents, slowly deliver, drop by drop, from a pipette held in the left hand, 2 cc. of magnesia mixture. With occasional shaking the author has found the precipitation of the phosphorus to be practically complete in two hours, but it is perhaps safest to allow the beaker to stand over-night.

[1] Author, *Chemical News*, No. 1114, p. 147.

[2] Including the preliminary operations.

Estimating the phosphorus.—The precipitate is filtered off, washed, dried, ignited, and weighed exactly in the manner described in the article on the magnesia process, but to the weight obtained on the balance one milligramme is added as a correction for the slight solubility of ammonium magnesium phosphate in dilute ammonia solution.

Theoretical Considerations.

Most of the points calling for explanation have been already dealt with in the magnesia process. The reason for slowly adding the precipitant whilst the liquid containing the phosphorus is in rapid motion is, that experience has shown that under these conditions the theoretical composition of the precipitate is best secured. The correction for the solubility of the precipitate—namely, one milligramme of pyrophosphate for each 50 cc. of solution—is usually also applied to the volume of washing liquid used. This procedure, however, the author's practice indicates to be inaccurate, inasmuch as the ammonium magnesium phosphate when once precipitated is practically insoluble in dilute ammonia solution. In precipitating phosphoric acid with magnesia, the presence of a large excess of ammonium chloride is advisable to prevent the possibility of a co-precipitation with the double phosphate of any $Mg(HO)$. The latter is soluble in $AmCl$.

Examples of Comparative results.

Jan 21, 1888.—Analysis of Basic Bessemer rail steel.

A. By Magnesia. Weight taken 5 grammes.

$$\begin{array}{rl} \text{Crucible + precipitate} = & 28{\cdot}0621 \\ \text{Weight of crucible} = & \underline{28{\cdot}0465} \\ & \cdot 0156 \quad \text{gramme } Mg_2P_2O_7 \\ & \underline{27{\cdot}93} \\ & 16758 \\ & 13965 \\ & \underline{2793} \\ & 5)\overline{\cdot 435708} \\ & \underline{0{\cdot}087\%} \quad \text{Phosphorus.} \end{array}$$

B. By Rapid Molybdate. Weight taken 2 grammes.

$$\begin{array}{rl} \text{Dish + precipitate} = & 32{\cdot}6394 \\ \text{Weight of dish} = & \underline{32{\cdot}5357} \\ & \cdot 1037 \quad \text{gramme yellow precipitate.} \\ & \underline{1{\cdot}63} \\ & 3111 \\ & 6222 \\ & \underline{1037} \\ & 2)\overline{\cdot 169031} \\ & \underline{0{\cdot}084\ \%} \quad \text{Phosphorus.} \end{array}$$

C. By Slow Molybdate. Weight taken 5 grammes.

$$\begin{array}{rl} \text{Dish + precipitate} = & 32{\cdot}8056 \\ \text{Weight of dish} = & \underline{32{\cdot}5375} \\ & \underline{0{\cdot}2681} \end{array}$$

$$\frac{\cdot 2681 \times 163}{5} = 0{\cdot}085\%\ \text{P.}$$

D. By the Combined Method. Weight taken 5 grammes.

$$\begin{array}{rl} \text{Crucible + precipitate} = & 28{\cdot}0619 \\ \text{Weight of crucible} = & \underline{28{\cdot}0462} \\ & \underline{\cdot 0157} \end{array}$$

$$\frac{\cdot 0167 \times 27{\cdot}93}{5} = 0{\cdot}093\%\ \text{P.}$$

Greatest difference in the four determinations $= 0{\cdot}009\ \%$

Estimation of Phosphorus in Special Steels.

In the cases of tungsten, high silicon, graphitic, or high chrome steels 6 grammes of the sample should be originally evaporated to dryness with nitric acid, and the solution of the dry mass in hydrochloric acid also should be evaporated to dryness and thoroughly baked. The dry mass of chlorides is dissolved up in 40 cc. of strong hydrochloric acid, and the solution transferred without loss to a 60 cc. flask, and when cold is diluted to the mark and thoroughly mixed: 50 cc. are then filtered off into a dry, graduated flask through a dry filter, and are carefully transferred to a 30-oz. registered flask, diluted, reduced, etc. in the manner already described for the preliminary operations.

Presence of arsenic.—In steels containing much arsenic the precipitates obtained by any of the four methods described will be probably contaminated with arsenic in the form either of yellow ammonio-arsenio molybdate or of ammonium magnesium arsenate, which on ignition yields a pyroarsenate exactly analogous to the phosphorus salt, namely, $Mg_2As_2O_7$. In arsenical steels, therefore, precipitate the phosphorus by means of ferric chloride and ammonium acetate in the filtrate obtained after precipitating the arsenic as sulphide in the manner described in the next article.

Estimation of Arsenic (Author.)

(Time occupied, about 1 day.)

Weight taken.—Dissolve 5 grammes of steel in 50 cc. of nitric acid, sp. gr. 1·2, evaporate to dryness, and bake the

residue exactly as in the preliminary operation for the estimation of phosphorus by the long method (see p. 118).

Dissolving the oxide of iron.—When cool, add down the lip of the covered beaker 50 cc. of strong hydrochloric acid, and very cautiously digest on the plate at the lowest possible temperature till the cake of oxide at the bottom of the beaker is entirely re-dissolved. During this operation the cover must be kept on, and *the temperature of the solution must never be allowed to approach boiling-point.*

Diluting and reducing.—As soon as the last piece of oxide of iron has passed into solution, add 200 cc. of hot water, and transfer the diluted solution without loss to a 30-oz. registered flask. The liquid is then neutralized with dilute ammonia, reduced with sulphurous acid, again neutralized and treated with a little more H_2SO_3, and boiled till the excess of SO_2 is expelled in the manner previously described on p. 118.

First precipitation of the arsenic.—Next pass through the hot liquid a brisk current of sulphuretted hydrogen from a Kipp's apparatus for at least fifteen minutes, till the precipitate flocks out, leaving the liquid clear or only opalescent with suspended finely-divided sulphur; then detach the precipitation-tube, leaving it in the flask, and allow the liquid to stand for at least half-an-hour.[1]

Filtering off the precipitate.—Collect the precipitate on a 110 mm. paper and thoroughly wash flask, precipitating tube, and filter quite free from iron salts with warm water containing 10 % by volume of strong hydrochloric acid solution.[2] The precipitate may be yellow when it consists of a mixture of free sulphur and sulphide of arsenic, As_2S_3,

[1] When only traces of arsenic are present the solution should be allowed to stand over-night.

[2] The phosphorus is estimated in the filtrate.

or it may be dark in colour owing to the presence of sulphide of copper, *CuS*, from copper previously existing in the steel.

Dissolving the precipitate.—Hang the funnel (having previously rinsed it from any external splashings of iron solution) inside a 20-oz. beaker, and treat the filter with the smallest possible quantity of warm dilute ammonia (heated in the flask in which the precipitation took place) till the sulphide has dissolved. The paper must be well washed with a fine jet of hot water, spread out on a clock glass, and any residue on it washed into the ammonia solution.

Formation of arsenic acid.—Cover the beaker and boil off most of the ammonia. Next add a slight excess of strong nitric acid, and boil down to a bulk of about 10 cc. till the precipitated sulphur is oxidized. The liquid should be quite free from iron, but may have a greenish tinge due to copper.

Precipitating the arsenic.—The acid liquid is made very strongly alkaline with ammonia, and the arsenic is precipitated with 2 cc. of magnesia mixture exactly as described for the precipitation of phosphorus by the combined method on page 125. With an occasional brisk shaking round the liquid deposits practically the whole of the arsenic in about four hours, but it is best to arrange the analysis so that the solution may stand over-night. Its bulk should not exceed 50 cc.

Weighing the precipitate.—The highly crystalline precipitate is filtered off, washed, dried, and ignited at a temperature just sufficient to burn off the carbon of the paper exactly in the manner described for the analogous phosphorus precipitate obtained in the magnesia method. The white residue is weighed as magnesium pyroarsenate containing 48·3 % of arsenic.

Estimation of Arsenic in Special Steels.

In the cases of tungsten and high chrome steels, weigh out 6 grammes of the drillings, and after gently dissolving up the dry oxide in hydrochloric acid, obtain 50 cc. of clear solution corresponding to 5 grammes of steel in the manner described on page 128. The liquid is then diluted, neutralized, reduced, etc. as usual. The whole of the tungsten is not separated, and the portion dissolved in the hydrochloric acid gives on passing the H_2S a considerable quantity of a blue-black precipitate of sulphide of tungsten. This has the advantage of quickly carrying down with it the whole of the arsenic, but the precipitate occupies a longer time in washing, and is partly dissolved by the treatment with ammonia. The sulphide thus dissolved is again partly re-precipitated in the ammoniacal solution, but throughout the process its presence may be ignored, as it finally remains in solution (in the strongly alkaline liquid from which the double arsenate is thrown down) as tungstate of ammonium.

When dealing with very high silicon steels, the procedure specified for pig-iron on page 193 should be followed.

Theoretical Considerations.

On dissolving the arsenical steel the arsenic is oxidized to arsenic acid H_3AsO_4, which on evaporating the solution and baking the residue remains fixed as ferric pyroarsenate $FeAs_2O_7$. During the re-solution in strong hydrochloric acid, boiling is carefully avoided to prevent the reduction of the re-formed arsenic acid to volatile arsenious chloride,

$AsCl_3$, which would escape. The action of the sulphurous acid reduces the arsenic to arsenious acid, in which form it is readily precipitated by sulphuretted hydrogen thus respectively—

$$H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4$$

Arsenic and sulphurous acids yield arsenious and sulphuric acids, and—

$$2\ H_3AsO_3 + 3\ H_2S = As_2S_3 + 6\ H_2O$$

Arsenious acid and hydrogen sulphide yield arsenious sulphide and water.

The treatment with ammonia converts the insoluble arsenious sulphide into soluble ammonium arsenite and thioarsenite, thus—

$$2\ As_2S_3 + 4\ AmHO = AmAsO_2 + 3\ AmAsS_2 + 2\ H_2O$$

On boiling the alkaline solution containing the arsenites with a slight excess of nitric acid, they are re-oxidized to arsenic acid, thus—

$$3\ HNO_3 + AmAsO_2 = H_3AsO_4 + AmNO_3 + N_2O_4$$

$$3\ HNO_3 + AmAsS_2 = H_3AsO_4 + AmNO_3 + 2\ S + N_2O_2$$

On adding ammonia to the nitric acid solution of the arsenic acid, the nitric acid is neutralized to ammonium nitrate, and ammonium arsenate is formed thus—

$$H_3AsO_4 + 3\ AmHO = Am_3AsO_4 + 3\ H_2O$$

On the addition of the magnesia mixture to the solution containing the ammonium arsenate an insoluble double arsenate is formed thus—

$$Am_3AsO_4 + MgSO_4 = AmMgAsO_4 + Am_2SO_4$$

On drying the crystalline double arsenate loses its water of crystallization, and on ignition is converted into magnesium pyroarsenate by a reaction exactly analogous to that already given for the corresponding phosphorus salt.

Example of a Determination.

0·2 gramme of a special arsenic steel, which the mean of two closely concordant estimations indicated to contain 1·56 % *As*, was added to 4·8 grammes of a steel free from arsenic. The amount of the element present therefore equalled 0·062 %.

The Result.

$$
\begin{array}{rl}
\text{Weight of crucible} + \text{precipitate} = & 27{\cdot}6392 \\
\text{Weight of crucible} = & 27{\cdot}6327 \\ \hline
Mg_2As_2O_7 = & {\cdot}0065 \text{ gramme.} \\
 & 48{\cdot}3 \\ \hline
 & 2415 \\
 & 2898 \\ \hline
 & 5)\,{\cdot}31395 \\ \hline
 & \underline{\underline{0{\cdot}063}}\ \%\ As
\end{array}
$$

The precipitate had a faint red tinge, due probably to traces of oxide of iron, which account for the above somewhat too favourable result.

Estimation of Tungsten (and Silicon).

This element is introduced into water-hardening steels in the proportion of about $2\frac{1}{2}$ %, whilst self-hardening steels contain about 10 %. Of the first-named class of steel, 2 grammes should be taken for analysis, but for the richer alloy 1 gramme is sufficient. The estimation is a tedious process, sometimes occupying a day and a half: water steels can always be drilled, but the self-hardening material has sometimes to be sampled for analysis in the form of crushed, or semi-crushed, fragments obtained from a small-sized bar.

The Method.

Dissolving.—Weigh out the steel into a 20-oz. covered beaker, dissolve by heating with 50 cc. of nitric acid, sp. gr. 1·2; boil down to low bulk, remove the cover, and place the beaker on a pipe-stem triangle.

First evaporation to dryness.—Next carefully evaporate to dryness, remove from the triangle, and bake well in the middle of the plate. Now allow the beaker to cool with the usual precaution, and dissolve up the dry mass of oxide of iron by boiling with 30 cc. of strong HCl, and again carefully evaporate to complete dryness.

Third evaporation.—Take up as before in 30 cc. of HCl, and gently vaporize the bulk of the acid, going down to about 5 cc.

Filtering.—Dilute with 50 cc. of water, and filter off the precipitate through a close-grained filter, contained in a 2¼-in. funnel, the latter being supported in a 100 cc. measuring-glass. Get through and throw away as much as possible of the clear iron solution before disturbing the precipitate with wash water, because some of the finely-divided WO_3 will probably pass through the pores of the paper, and the filtrate must be re-passed through the filter till the interstices of the latter are filled up and the liquid comes through quite clear. This is readily ascertained by holding up the measuring-glass to the light, and carefully examining the fluid contents for suspended matter. The paper and precipitate must now be washed *quite free from ferric chloride*[1] with cold, very dilute (5 %) hydrochloric

[1] In rich alloys the final residue may be examined for Fe_2O_3 by fusing it with $HKSO_4$. If present, the weight must be estimated colorimetrically and deducted. The aqueous extract from the fusion

acid and cold water. After drying in the usual manner, the filter is ignited in a clean, tared platinum crucible, and the latter, when cold, is re-weighed. The increase is $(x\ WO_3 + y\ SiO_2)$.

Treatment with HF.—To the ignited mass in the crucible add 2 cc. of *pure*[1] aqueous hydrofluoric acid. The latter is quietly evaporated off in the draught cupboard, and the crucible is re-ignited, cooled, and re-weighed. The loss from the second weighing $= SiO_2$, containing 46·7 % Si; the increase over the first weighing of the crucible $= WO_3$, containing 79·3 % of tungsten.

Theoretical Considerations.

On dissolving the steel in nitric acid when only about 3 % tungsten is present, it passes into solution as tungstic acid, probably forming a compound somewhat analogous to that produced under the same conditions by silicic acid (see p. 60). If, however, 10 % tungsten is present, some of the WO_3 separates as an insoluble yellow precipitate. The conversion by baking of the ferric nitrate into oxide also determines the decomposition of the organic carbon compound, which, had the preliminary solution, as often advocated, been made in aqua regia, would have separated in a slimy condition, and thus have rendered still slower an already tedious filtration. The second evaporation to dryness and the third to low bulk with HCl ensure the complete separation of the tungstic acid, some of which, with only one or two evaporations, is liable to remain

---

is made up to a known volume, and the iron in a portion of the filtered liquid is determined as described on p. 77.

[1] The aqueous acid should leave no residue on evaporation.

dissolved in the hydrochloric acid solution. The treatment with hydrofluoric acid of the mixed residue of tungstic anhydride and silica brings about a volatilization of the latter, thus—

$$SiO_2 + 4\,HF = SiF_4 + 2\,H_2O$$

Silica and hydrogen fluoride yield gaseous fluoride of silicon and water. The alleged liability of some of the WO_3 to volatilize with the silicon unless sulphuric acid is present has no foundation in fact.

The method found in most text-books for separating tungstic and silicic anhydrides is based upon the solubility of WO_3 and the insolubility of SiO_2 in hot ammonia solution. This process is absolutely worthless—

(*a*) Because strongly baked WO_3 is not always completely soluble in ammonia.

(*b*) Because SiO_2 obtained from H_4SiO_4 by evaporation of a hydrochloric acid solution is almost completely soluble in hot ammonia solution.

Mr. Lawrence Dufty has made a very complete research upon this point. The paper embodying the results obtained was read before the Sheffield Technical School Metallurgical Society, and from that communication the results tabulated below are extracted.

Samples of tungsten steel were tested as follows:—

Two grammes (in the case of C, 1 gramme) were dissolved in aqua regia, evaporated to dryness, re-dissolved in hydrochloric acid, again evaporated to dryness, and baked. The mass was taken up in hydrochloric acid. The silicic and tungstic oxides were filtered off, and washed free from iron with dilute hydrochloric acid and water. The precipitates were next treated on the paper with 50 cc. of hot dilute ammonia (1 volume of 880 to 3 of water). The alkaline filtrate was evaporated to dryness in a platinum

dish, the residue after ignition being weighed as WO_3. The filter-paper and the undissolved matter upon it were also ignited, and the residue was weighed as SiO_2. The results are set out in the following table:—

TABLE I.

Sample.	Gramme.		Per cent.	
	SiO_2.	WO_3.	Silicon.	Tungsten.
A	0·0024	0·0164	0·05	0·65
B	0·0092	0·0800	0·21	3·17
C	0·0098	0·1664	0·45	13·19

The residue usually supposed to be WO_3 was treated with aqueous hydrofluoric acid, and after the latter had been evaporated off, was re-weighed, the loss in weight being silica dissolved out by the ammonia treatment (see next table).

TABLE II.

Sample.	Loss = SiO_2.	Loss = Silicon %.	Residue of pure WO_3, gramme.
A	0·013	0·30	0·0034
B	0·009	0·21	0·0710
C	0·008	0·37	0·1584

The correct weights and percentages are therefore as follows:—

TABLE III.

Sample.	Gramme.		Per cent.	
	SiO_2.	WO_3.	Silicon.	Tungsten.
A	0·0154	0·0034	0·36	0·13
B	0·0182	0·0710	0·42	2·81
C	0·0178	0·1584	0·83	12·56

A comparison of Tables I. and III. will strikingly illustrate the errors of the ammonia process.

Samples of ordinary steel containing no tungsten were treated exactly as before, the dried chlorides being baked in the centre of the hot plate for two hours. The quantities used were—

5 grammes of sample D, which contained 0·28 % *Si*.
2 „ „ E, „ „ 1·21 „

The results obtained are tabulated below.

TABLE IV.

Sample.	Gramme SiO_2.		Silicon per cent.		Total Silicon %.
	In filtrate.	On filter paper.	Dissolved.	Not dissolved.	
D	0·0220	0·0079	0·205	0·073	0·278
E	0·0343	0·0182	0·800	0·424	1·224

Gravimetric Estimation of Chromium as Oxide (Author[1]).

Re-agent required.

Fusion mixture.—Intimately mix 100 grammes each of pure dry powdered potassium nitrate, potassium carbonate, and sodium carbonate; preserve the mixture in a well-stoppered bottle.

The Process.

(Time occupied, about 1 day.)

Weight taken.—Weigh out into a covered 20-oz. beaker 2·4, 1·2, or ·6 grammes of the steel according to its richness in chromium. The weight last mentioned is suitable for a steel containing say 6 % of the metal.

[1] *Chemical News*, 1880, No. 1098.

Dissolving.—Add in the case of 2·4 grammes of steel 30 cc. of strong hydrochloric acid; gently heat on the plate till the drillings have dissolved, and then boil the liquid down to low bulk. The evaporation is then slowly continued with the cover off so as to obtain the chlorides in a compact, dry cake at the bottom of the beaker. The residue must not be baked, but is merely taken quietly to dryness in such a manner that the cover and sides of the beaker are free from splashings.

Pulverizing the chlorides.—Allow the mass to go cold, and then, with the aid of a steel spatula the brittle cake may be cut up into several easily detached pieces, which are carefully transferred to a 3-in. porcelain dish. Any strongly adhering particles of chloride which cannot be brushed out are dissolved in a very few cc. of strong hydrochloric acid, the covered beaker being heated on the plate till all soluble matter is taken up. The solution, together with any insoluble residue, is transferred with the aid of a fine jet of water into a deep 3-in. platinum dish, into which any chlorides adhering to the spatula are also washed. The dish is then placed over a little beaker of boiling water, and its contents, which should never exceed 15 cc., are evaporated to dryness. Whilst the evaporation is proceeding the main portion of the chlorides in the porcelain dish (which should be placed on a sheet of glazed white paper) is reduced to a fine powder by means of a little round-headed pestle made out of ¼-in. diameter glass rod, after which the pestle is cleaned from adhering chlorides by means of a pen blade and camel's hair brush. When the contents of the platinum dish are dry it is taken off the beaker, and is well wiped outside.

Fusion.—Carefully transfer the powdered chlorides from the porcelain to the platinum dish, well rinsing the latter

by means of the pestle with several fractions of 30 grammes of fusion mixture, after which the remainder of the latter is added to the chlorides, and the whole is intimately mixed with the pestle into a uniformly tinted powder. After brushing the pestle gently tap down the mixture, cover the dish, and place it on a pipe-stem triangle supported on a tripod, and, cautiously at first, heat the mass over a good Bunsen burner for about fifteen minutes till the excess of alkalies is quite liquid; then remove the lamp.

Extracting the fusion.—When moderately cool place the dish and cover in a 20-oz. beaker containing 200 cc. of nearly boiling water: in two or three minutes, by means of a glass rod, tilt up the cover so that a portion can be washed, take hold of the cover by the washed edge, lift it out of the solution, well rinse it all over, and remove. By means of the glass rod occasionally rotate the dish till the alkaline salts have all dissolved, and the oxide of iron is completely detached in the form of a red powder. The crucible is then washed and removed by means similar to those employed in the case of the cover. Thoroughly stir the liquid with a glass rod, and wash and remove the latter.

Filtering off the iron and manganese.—Transfer the hot liquid and precipitate in the beaker without loss to a 301 cc. graduated flask marked low down in the neck, and dilute to about 301·5 cc. By means of a long chemical thermometer thoroughly stir the yellow liquid till uniform in colour; withdraw the thermometer just clear of the meniscus, till the latter by the contraction of the liquid reaches the mark. Note the temperature of the solution, allow the oxide of iron to settle for a few minutes, and then through a dry double paper contained in a 2¼-in. ribbed funnel filter off into a 250 cc. dry graduated flask about

249·5 cc. of the perfectly clear yellow liquid; remove the funnel, and heat the flask on the plate till its contents approach the previously noted temperature. Then, by means of the thermometer, throw out drops of the fluid till 250 cc. at the original temperature are obtained.

Reducing.—Pour and wash out every trace of the solution from the flask into a 20-oz. covered beaker, and add down the lip 25 to 35 cc. of strong hydrochloric acid till no more CO_2 is evolved, and the colour of the liquid has changed from yellow to clear green. Bring the liquid to boiling, and keep it in ebullition till the brown fumes in the upper part of the beaker have disappeared.

First precipitation.—Next, very cautiously, a little at a time, add to the gently boiling liquid down the lip of the beaker dilute ammonia solution till the hydrochloric acid is neutralized, a permanent pale-green precipitate is obtained, and a very faint excess of ammonia is present. Then remove the beaker to a cooler part of the plate, and digest it just short of boiling till the precipitate has collected into flocks and the liquid is crystal clear.

Filtering.—Allow the precipitate to settle, and do not disturb it more than necessary till most of the clear filtrate has been poured through a 110 mm. paper. Then throw the precipitate on the filter, rinse out the beaker with hot water, wash the edges of the filter-paper once, and allow it to drain.

Re-dissolving the precipitate.—Hang the funnel inside the beaker in which the precipitation took place, and by means of hot, slightly diluted hydrochloric acid, dissolve the precipitate, using the smallest possible quantity of solvent, and well wash the paper with a fine jet of cold water. The filter is then put under cover till required for re-filtering the solution if necessary.

Separating SiO_2 and WO_3.—Cover the beaker containing the green chloride solution, briskly boil down to low bulk, and then, without the cover, quietly evaporate the liquid till green crystals are deposited. (These, if further heated, turn red, and are re-dissolved with difficulty.) Add 5 cc. of strong hydrochloric acid, and heat till the crystals are re-dissolved, if necessary adding a little water. The liquid is then carefully examined to ascertain if any silica or yellow tungstic acid has precipitated. If so, the liquid, after diluting with 20 cc. of water, is passed through the paper previously used into a clean 20-oz. beaker, and the paper is then exhaustively washed. If, however, the liquid is clear, which is often the case, it is diluted to 200 cc., and heated to boiling in the covered beaker.

Re-precipitating the chromium.—The chromium is next precipitated with well-diluted ammonia (1 of 880 to 3 of water) exactly as described for the first precipitation.

Final filtration and washing.—Filter off on a 110 mm. pure paper contained in a 2½-in. funnel as before, but in the present case every particle of precipitate is carefully detached by means of a policeman, and the beaker is thoroughly rinsed out with hot water. The paper is thrice washed round the edges with nearly boiling water without disturbing the precipitate, which, if stirred up by a too vigorous application of the jet, is liable to a small extent to pass through the pores of the paper. After the last washing, allow the filter to drain: the filtrate should be crystal clear.

Weighing.—The paper is detached from the funnel and dried in the usual manner. It is strongly ignited in a tared platinum crucible, and when quite cold the latter is removed from the desiccator and re-weighed. The increase is Cr_2O_3, containing 68·5 % of metal.

Example of a trial Determination.

To 2·4 grammes of a steel free from chromium 0·0678 gramme of pure dry $K_2Cr_2O_7$ was added, corresponding to 1 % of chromium.

Result.

```
     Crucible + ppt. = 28·6320
Weight of crucible = 28·6034
                      ·0286
                       68·5
                      1430
                     2288
                    1716
                  2)1·95910
                    0·97955 say 0·98 % Chromium.
```

Theoretical Considerations.

The preliminary solution and evaporation to dryness with hydrochloric acid yields the mixed chlorides of the metals iron, chromium, and manganese, together with silica, traces of phosphate and sulphate of iron, and a little carbonaceous matter. The action of the fusion mixture converts the iron to Fe_2O_3 absolutely insoluble in water, the chromium to a mixture of the yellow chromates of potassium and sodium K_2CrO_4 and Na_2CrO_4, the manganese to green alkaline manganates K_2MnO_4 and Na_2MnO_4.

The silica is converted into alkaline silicates (see p. 278), whilst any sulphates or phosphates present form respectively the sulphates and pyrophosphates of potassium and sodium, *e.g.* Na_2SO_4 and $Na_4P_2O_7$. The potassium nitrate is converted into nitrite KNO_2. On extracting the fusion in hot water the alkaline manganates decompose, and the manganese is totally precipitated as hydrated dioxide.

The alkaline chromates, silicates, sulphates, and pyrophosphates pass into solution together with the excess of carbonates and the potassium nitrite. On acidifying the yellow filtrate with hydrochloric acid, the liquid for a moment assumes a much deeper yellow colour, owing to the formation of bichromates, thus—

$$2\,K_2CrO_4 + 2\,HCl = K_2Cr_2O_7 + 2\,KCl + H_2O$$

The hydrochloric acid then liberates nitrous acid from the potassium nitrite, when the bichromate is reduced to green chromic chloride with evolution of nitrous fumes, whilst the pyrophosphates are converted into orthophosphates. On the addition of ammonia, green chromic hydrate is precipitated thus—

$$CrCl_3 + 3\,AmHO = Cr(HO)_3 + 3\,AmCl$$

The above hydrate is soluble in a large excess of ammonia, hence the necessity for using only a faint excess. With the precipitate will be found any traces of phosphoric acid P_2O_5 combined with a portion of the hydrate, but in steels containing only about 0·05 % P, the residue of phosphorus not evolved as PH_3 (amounting to about 20 % of the total P present) causes only a trifling + error,[1] which, in fact, seems to compensate for the small loss of chromium occurring during the analysis. It is hardly necessary to state after the above remarks, that the fusion mixture employed should be absolutely free from phosphates. In steels in which the phosphorus is somewhat high and the percentage of chromium present is small, the hydrate method should not be used, but the process described in the next article should be employed. The

[1] In a steel containing about 0·1 % of P, the error from the phosphorus oxidized to phosphoric acid (P_2O_5) during the dissolution of the steel in HCl will equal on 2 grammes of steel 0·03 to 0·04 % Cr, equivalent to about 1 milligramme of P_2O_5.

reason for re-precipitating the chromic hydrate is, that it may be contaminated with a little silica, and is invariably impure with small quantities of alkaline salts, from which, on the second precipitation, it is free. The extra 1 cc. over the 300 cc. of liquid containing the chromium in 2·4 grammes of steel is a correction for the volume of the ferric oxide, and for a slight concentration of the solution by evaporation during filtration.

Influence of Special Elements on the Analysis.

Copper and nickel both remain with the oxide of iron in the respective forms of CuO and NiO. When tungsten is present, it totally passes into solution with the yellow chromates as alkaline tungstate, but by reason of its partial solubility in hydrochloric acid and its complete solubility in ammonia, the tungstic acid is completely got rid of during the analysis, and the final precipitate is free from it. The case of aluminium requires special treatment, which will be described at the end of the next article.

GRAVIMETRIC ESTIMATION OF CHROMIUM AS PHOSPHATE. (Author and Hardy.[1])

(Time occupied, about 1¼ days.)

This process should always be employed for the gravimetric estimation of small quantities of chromium in steels containing say 0·1 % *P*. It is also useful in cases of dispute as an alternative method of determination.

[1] *Chemical News*, 1888, No. 1482.

Re-agent required.

10 % *solution of sodium phosphate.*—Dissolve 25 grammes of ordinary phosphate of soda (Na_2HPO_4, 12 Aq) in 250 cc. of water. The filtered liquid is best kept for use in a green glass bottle with an india-rubber stopper.

The Process.

The method is carried out exactly in the manner described for the hydrate process, except that before the first precipitation 10 cc. of the 10 % solution of phosphate of soda are added. Also the precipitate is weighed as $Cr_6P_4O_{19}$ containing 42·48 °/$_o$ Cr. The weighing should be made in a covered crucible (in the manner described on p. 68 for the determination of silicon), because the basic phosphate is somewhat hygroscopic.

Theory of the Process.

When phosphoric acid P_2O_5 and salts of chromic oxide Cr_2O_3 are in solution together, if the former be largely in excess the precipitate obtained on digesting the liquid with a slight excess of ammonia is uncertain in composition. It may be the normal salt $Cr_2P_2O_8 = (Cr_2O_3, P_2O_5)$, but is sometimes a mixture of normal and basic salt, and sometimes a mixture of normal and acid phosphate, but in the presence of the theoretical amount or of a moderate excess of P_2O_5 chromic oxide is completely precipitated as a definite basic phosphate $Cr_6P_4O_{19}$.

The data upon which the foregoing statements are

founded are set forth in the following table extracted from the original memoir published in the *Chemical News.* Various weights of pure dry $K_2Cr_2O_7$ in dilute hydrochloric acid solution were reduced by means of sulphurous acid. The chromium was then precipitated by a faint excess of ammonia in the presence of varying amounts of phosphoric acid introduced by means of a solution of sodium phosphate carefully standardized by magnesia. Results—

Ratio of Molecules.		Grammes.				
Cr_2O_3.	P_2O_5.	Cr_2O_3.	P_2O_5.	Precipitate obtained.	Theory.	
					$Cr_6P_4O_{19}$.	$Cr_2P_2O_8$.
—	—	0·0265	0·0221	0·0430	0·0430	—
—	—	0·0258	0·0221	0·0415	0·0418	—
—	—	0·0516	0·0387	0·0830	0·0837	—
—	—	0·0258	0·0600	0·0500	—	0·0500
—	—	0·0546	0·0800	[1]0·0990	0·0885	0·1056
3	2	0·0389	0·0240	0·0625	0·0629	—
1	1	0·0258	0·0240	0·0420	0·0417	—
1	16	0·0258	0·3840	[2]0·0560	0·0417	0·0500
1	32	0·0258	0·7680	0·0496	—	0·0500

[1] Indefinite basic phosphate. [2] Indefinite acid phosphate.

Therefore, in the first precipitation, when a large excess of sodium phosphate is present, the constitution of the phosphate is uncertain, except that it will certainly contain P_2O_5 somewhat in excess of that necessary to form $Cr_6P_4O_{19} = (3\ Cr_2O_3,\ 2\ P_2O_5)$; but on the second precipitation conditions are secured under which the results obtained in the above table prove that the definite basic phosphate is thrown down, whilst the small excess of P_2O_5 combines with the free ammonia present to form Am_3PO_4, which may be proved by well washing a first precipitate, and adding a nitric acid solution of ammonium molybdate to the filtrate from the second precipitate.

Estimation of minute quantities of Chromium.

In estimating percentages of chromium falling below 0·1 %, weigh out 12 grammes of steel, and obtain the chromium associated with a comparatively small quantity of iron exactly in the manner described for obtaining the second precipitate in the estimation of aluminium on page 169, of course adding enough phosphate of soda to precipitate chromium equivalent to ·1 % of 12 grammes, using rather more sulphurous acid and ammonium acetate, and precipitating from a more dilute solution. The paper containing the precipitate is, after drying, ignited in a small platinum dish, the residue is mixed with 2 or 3 grammes of fusion mixture, and fused in the usual manner. The extract is made up to 120 cc., 100 cc. are filtered off, and on this volume the analysis is proceeded with as already described; the chromium is weighed as basic phosphate, and the result calculated on 10 grammes of steel. Mr. J. E. Stead has published results[1] which seem to indicate that chromium is almost universally present in small quantities in British iron and steel products. Mr. Stead tabulates percentages as low as 0·006, but as the results were obtained by an indirect volumetric process, involving the use of re-agents so readily reduced as potassium permanganate, and so easily oxidized as ferrous sulphate, the author is of opinion that the unavoidable errors of analysis in the method employed are *per se* capable of indicating an apparent % of chromium so minute as that quoted. Deservedly high as is the reputation of Mr. Stead as a steel analyst, chemists should not absolutely accept his volumetric results till they have been confirmed

[1] *Journal of the Iron and Steel Institute,* 1893, No. 1, p. 168.

by the above process, in which a precipitate of pure phosphate of chromium is actually seen and directly weighed.

Comparative Advantages of the Hydrate and Phosphate Methods.

In all Swedish steels and in high-class English Bessemer and open-hearth products, the hydrate process is undoubtedly the best to use; the precipitate is less bulky, more soluble in hydrochloric acid, less liable to pass through the paper on washing, and, if the hydrochloric acid solution of the first precipitate is inadvertently carried to complete dryness after the evaporation, the baked chloride is much more easily re-dissolved than the phosphate under similar conditions. Finally, the hydrate is not hygroscopic after ignition. On the other hand, the phosphate precipitate is less liablo to take up SiO_2 when unwittingly boiled in a new beaker, and is not so soluble in any accidentally added large excess of ammonia. It has also the advantage of giving a larger weight of precipitate for a corresponding percentage of metal. The author's experience in working upon 0·5 grammes of chromium free steels, into which 6 % of metal in the form of $K_2Cr_2O_7$ had been introduced, has been, that the hydrate results averaged 5·95 % *Cr*, whilst the phosphate determinations indicated 6·05 %. In working upon steels containing say 2 % of chromium, duplicate estimations on different weights of drillings agree to about 0·02 %. Mr. William Galbraith has stated in a paper to be subsequently referred to, that gravimetric estimations of chromium are usually seriously high. Mr. Galbraith's view on this point is an altogether mistaken one. During the last thirteen years the author's experience

of gravimetric estimations of chromium, made not only upon known quantities, but upon samples representing hundreds of tons of chrome pig-iron, and thousands of tons of chrome steel, has proved that properly-conducted gravimetric determinations of chromium invariably give accurate and concordant results.[1]

Determination of Chromium in Aluminium Steels.

When aluminium is present in a steel in which the chromium is being estimated by either of the foregoing methods, part of it will be found in the yellow solution of the chromates as sodic aluminate $(NaAl)_2O_4$, whilst a portion remains with the ferric oxide as Al_2O_3. Unless separated, the portion present with the chromium will be precipitated as hydrate or phosphate, thus giving too high a result. The separation is easily and completely effected thus: To the total yellow extract containing the precipitates of iron and manganese add 10 cc. of a saturated solution of re-sublimed ordinary ammonium carbonate ($3\,Am$, $2\,CO_2$, HO), then pass through the liquid for at least fifteen minutes a brisk current of washed CO_2 generated from marble and hydrochloric acid. The aluminium is totally precipitated as an indefinite, basic carbonate, and is then filtered off with the iron and manganese. The principle of the reactions involved may be formulated as follows—

$$Na_2CO_3 + (Al_2O_3, Na_2O) + 4\,AmHCO_3 + H_2O =$$
$$4\,NaHCO_3 + Am_2CO_3 + 2\,AmHO + Al_2O_3$$
$$2\,AmHO + CO_2 = Am_2CO_3 + H_2O$$

[1] As has already been pointed out by Mr. Stead, the precipitation of chromium by diffused $BaCO_3$ is valueless as a quantitative process.

The sodic aluminate and the excess of normal sodium carbonate present in the liquid after the fusion form acid or bi-carbonate of soda (in which alumina is insoluble), together with normal ammonium carbonate and free ammonia, in which the alumina remains dissolved; but on the conversion of the free ammonia into ammonium carbonate by the passage of CO_2, the alumina is totally precipitated in combination with some carbonic acid.

Volumetric Estimation of Chromium (Galbraith).

This process was devised some fifteen years ago by Mr. W. Galbraith for estimating the chromium in pig-iron, and that alloyed in small quantity with steel. For the latter purpose up to 0·25 % *Cr*, the method originally published, answered well, but when applied to chrome-pig or to steel containing a considerable percentage of the metal, the results obtained were always low, sometimes seriously so, from the following causes:—

(*a*) In pig-irons the chromium present was not completely dissolved by the dilute sulphuric acid used for a solvent.

(*b*) No precaution was given with reference to the vital point of the volume to which the solution must be diluted, to ensure the oxidation of the chromic oxide [existing in the sulphate (Cr_2O_3, 3 SO_3)] to chromic anhydride CrO_3.

(*c*) The amount of permanganate of potash specified was about six times too much.

The error introduced under heading (*a*) is too obvious to need explanation. The chromium missed under heading

(*b*) escaped estimation, owing to the fact that in a not sufficiently diluted sulphuric acid solution some chromic oxide remained unoxidized to the acid-forming oxide. The loss under heading (*c*) was brought about by the unnecessarily large amount of manganic precipitate formed, carrying down with it some of the chromium. The above facts have recently been recognized by Mr. Galbraith, and in the *Journal of the Iron and Steel Institute*, 1893, No. 1, page 150, he amended his process for completely soluble steels as follows :—"The process thus becomes—Dissolve in sulphuric acid (1 in 6), add permanganate, and boil till precipitate is black ; then dilute and make alkaline with caustic soda ; filter, wash, acidulate filtrate, and treat as before with ferrous salt and potassium bichromate."

The author has been unable to work the amended process—(1) because the precipitate never becomes black, but is of a deep rich brown colour ; (2) when working say upon 2 grammes of steel, on making the oxidized solution alkaline with sodic hydrate, the whole of the iron is thrown down, yielding a bulky precipitate, almost incapable of being properly washed.

Modified method.—The following modification worked out by the author preserves the simplicity of the original process, and to a great extent eliminates its errors. The results obtained on strictly following out the empirical conditions herein laid down are practically accurate, at any rate in steels containing up to 3 % of chromium.

Re-agent required.

Standard solution of $K_2Cr_5O_7$.—This is made by dissolving 2·8310 grammes of pure, recently dried crystals of potassium bichromate in distilled water, and making up

the solution to 1000 cc. The liquid is then standardized by dissolving 0·1618 gramme of Swedish bar-iron (99·8 % *Fe*) in 70 cc. of dilute sulphuric acid (1 in 7). On titrating the acid solution of ferrous sulphate with the ferricyanide indicator (see p. 86), exactly 50 cc. of bichromate solution should be required. The liquid is corrected for strength or weakness in the manner exemplified on p. 89.

The Process.

(Time occupied, about 1½ hours.)

Weight taken.—Weigh out 2 grammes of the steel into a clean dry 10-oz. flask.

Dissolving.—To 60 cc. of water contained in a small beaker add 10 cc. of pure, strong sulphuric acid, and pour the hot mixture into the flask. The contents of the latter, after covering the mouth with a watch-glass, are briskly boiled till the drillings are dissolved, and the acid has become so concentrated that white crystals of anhydrous sulphate of iron begin to precipitate.

Diluting.—Rinse the watch-glass, dilute the solution with 100 cc. of hot water, and bring the liquid to incipient boiling.

Oxidizing the chromium to CrO_3.—Remove the flask from the plate, dissolve in the solution, a few crystals at a time, pure potassium permanganate, well shaking round the fluid after each addition till the iron is oxidized to ferric sulphate, and a slight, pale-brown permanent precipitate is produced. About 1¼ grammes of the crystal will be required to reach this stage. Next add, weighed roughly, 0·2 gramme more of the permanganate crystals

and shake the liquid round till they have dissolved, producing a dark-brown precipitate; then rinse down from inside the neck of the flask any adhering fragments of permanganate; the contents of the flask are then boiled for five minutes and removed from the plate.

Filtering.—Allow the precipitate to settle somewhat, and, slowly at first, pour the solution through a *pure*[1] 110 mm. filter contained in a $2\frac{1}{4}''$ funnel. The rich purple-brown precipitate is then thrown upon the filter, the flask is well rinsed out, and the precipitate and paper are washed with hot water till the filtrate is colourless. The latter is received into a perfectly clean 14-oz. conical beaker. The filtration and washing occupy only from five to ten minutes.

Titrating.—When weighing out the chrome steel there should also be weighed out into a clean, dry 12-oz. flask 0·3236 gramme of Swedish Lancashire hearth bar-iron, in which on analysis the iron by difference should be practically 99·8 %. As soon as the filtration of the chromic solution is commenced, add to the flask containing the iron a mixture of 10 cc. of strong sulphuric acid with 60 cc. of water, and boil the contents of the flask, after covering

[1] Thick filters of impure paper are liable to reduce a little chromic acid to chromic oxide during the filtration, but the author has not been able to detect any practical difference in the results obtained when ashless papers are used, and those registered on a filtrate passed —as suggested by Mr. Hogg—through recently-ignited asbestos. If the latter is used, 2·4 grammes of steel may be employed, using 0·25 gramme excess of permanganate, and titrating five-sixths of the total liquid. The latter is filtered through an asbestos plug packed in the shoulder of a small piece of combustion tubing 1″ in diameter, but drawn out at one end to an inside diameter of $\frac{1}{8}''$; as much as possible of the liquid is passed through the plug before throwing much precipitate upon it.

the latter with a watch-glass. The known quantity of ferrous sulphate in sulphuric acid solution, which must be quite colourless, will thus be ready shortly after the washing is completed. When the last particle of iron is dissolved, remove the flask from the plate, and pour into it the perfectly clear chromic solution from the conical beaker, well rinsing out the latter.[1] The excess of iron is then determined by the standard bichromate solution, delivered from a 50 cc. burette, exactly in the manner described for manganese on p. 86; each cc. remaining in the burette equals 0·05 % *Cr*. The 50 cc. of standard solution are therefore capable of estimating a maximum of 2·5 % *Cr*. For steels up to 5 % double the weight of iron (0·3236) is employed, then each cc. left out of 100 cc. of the bichromate solution also equals 0·05 % *Cr*.

Example of Titration.

Working on the quantities first given, 23·2 cc. of the standard solution were required to oxidize the excess of ferrous iron, then $50 - 23{\cdot}2 = 26{\cdot}8$, and $26{\cdot}8 \times {\cdot}05 = 1{\cdot}34$ % of chromium.

Theoretical Considerations.

The reason for boiling the sulphuric acid solution of the steel till sulphates precipitate, is to ensure the decomposition of separated flocks of black chromium carbide, which resists the attack of the more dilute acid. On adding the first and main portion of permanganate to the solution the iron is oxidized from ferrous to ferric sulphate thus—

$$2\,KMnO_4 + 2\,FeSO_4 + 4\,H_2SO_4 = Fe_2(SO_4)_3 + K_2SO_4 + 2\,MnSO_4 + 4\,H_2O$$

[1] Never pour the iron solution into the chromic liquid, because the former may then become slightly oxidized by the air.

The last-added $\frac{2}{10}$ths of a gramme of permanganate by a reaction not well understood, oxidizes the chromium existing as chromic oxide Cr_2O_3—in the chromic sulphate $Cr_2(SO_4)_3 = (Cr_2O_3, 3\ SO_3)$—to chromic acid H_2CrO_4. Potassium sulphate is also formed, and a dark-brown precipitate consisting probably of hydrated MnO_2 mixed with hydrates of the higher acid-forming oxides of manganese. The chromic acid acts upon the ferric sulphate thus—

$$2\ H_2CrO_4 + 6\ FeSO_4 + 6\ H_2SO_4 = Cr_2(SO_4)_3 + 3\ Fe_2(SO_4)_3 + 8\ H_2O$$

The reaction of the bichromate solution upon the acid ferrous sulphate is formulated on p. 88, and from the examples there given, the calculation of the standard solution used in the present case should be obvious. Some chemists use for ferrous iron a weighed quantity of ferrous sulphate or ammonio-ferrous sulphate crystals. Sometimes the salts are made up in dilute sulphuric acid solution (1 in 10) into standard liquids. The above proceedings involve a pre-supposition of the perfect purity of the bichromate. It is therefore better to standardize from pure metallic iron, concerning which no doubt can exist. When standard acid solutions of ferrous salts are employed, they should be frequently checked by a standard bichromate solution, to ascertain that no atmospheric oxidation has occurred. The weight of uneffloresced green crystals of ferrous sulphate ($FeSO_4$, 7 H_2O) necessary to dissolve in dilute sulphuric acid as an equivalent for the weight of metallic iron used in the foregoing process will be 1·603 grammes. If made up into a standard solution 32·06 grammes of salt must be dissolved in about 700 cc. of cold dilute sulphuric acid (1 in 7), and the liquid made up to 1 litre. 50 cc. of this solution should be equivalent to 0·1618 gramme of Swedish iron. In the case of ammonio-

ferrous sulphate ($FeAm_2(SO_4)_2$, 6 H_2O), which is perhaps the better salt to employ, 2·261 grammes of crystals will be required per estimation, or if made up into a standard solution containing in 50 cc. ferrous sulphate equivalent to 0·1618 gramme of Swedish iron, 45·22 grammes of the salt must be contained in 1000 cc. of dilute sulphuric acid.

Volumetric Estimation of Chromium (Stead[1]).

Mr. Stead has devised the following modification of the permanganate process, which in the author's hands has yielded excellent results, closely agreeing with those obtained by the gravimetric processes and the preceding method when working upon completely soluble chrome steels.

The Process.

(Time occupied, about 1½ hours.)

Weight taken.—Weigh out 2 grammes of drillings into a 40-oz. flask.

Dissolving.—This is effected exactly as in the process last described.

Diluting.—Take up the separated sulphates by diluting the solution with 300 cc. of hot water.

Oxidizing.—Bring the liquid to boiling, and add a warm saturated solution of potassium permanganate till a brown precipitate is produced, and the boiling liquid is decidedly and permanently coloured with permanganate.

Dissolving up the manganic precipitate.—Add little by little to the still boiling fluid strong *HCl* solution till the

[1] *Journal of the Iron and Steel Institute*, 1893, No. 1, p. 158.

precipitate is dissolved, and a clear, rich yellow-red liquid is obtained: 70 to 90 cc. of the fuming acid will be required. Then add 100 cc. of hot water.

Boiling off the chlorine.—The liquid is now briskly boiled for about 20 minutes, till absolutely free from any smell of chlorine. The disengagement of the latter is facilitated by dropping into the flask a pinch of recently-ignited white sand.

Titrating.—The chlorine-free liquid is then added to an excess of ferrous sulphate, the liquid is titrated, and the percentage of chromium is calculated exactly as described for the last method, the dilute sulphuric being added to the iron contained in a 40-oz. flask, when the operation of boiling off the chlorine is nearly completed.

Theoretical Considerations.

Most of the reactions are identical with those occurring in the last process. The precipitated MnO_2 is, however, in the present case converted into manganous chloride with evolution of chlorine, thus—

$$2\,MnO_2 + 4\,HCl = MnCl_2 + 2\,Cl + 2\,H_2O$$

The sand mechanically assists the evolution of chlorine gas from the solution. If any free chlorine is left in the liquid it will oxidize the ferrous sulphate thus—

$$2\,FeSO_4 + 2\,Cl + H_2SO_4 = Fe_2(SO_4)_3 + 2\,HCl$$

Of course giving a result higher than the truth, the oxidizing power of the chlorine being registered as due to chromic acid. The solution in the present process is largely diluted to avoid the reduction of some of the chromic acid to chromic chloride, which takes place in a liquid strongly acid with HCl thus—

$$H_2CrO_4 + 6\,HCl = CrCl_3 + 3\,Cl + 4\,H_2O$$

Comparative Consideration of the Gravimetric and Volumetric Methods.

Where only few estimations have to be made, and time is not a condition of vital importance, the gravimetric is the most reliable process to employ, particularly in the analysis of steels containing a very high percentage of chromium, which are not completely dissolved by sulphuric acid, leaving a black residue of carbide of chromium. In disputed cases, volumetric results should be invariably confirmed by a carefully conducted direct assay. On the other hand, the volumetric process, certainly in steels containing up to 3 % of chromium, gives practically accurate results, which have the advantage of being very promptly obtained, in a manner far less tedious than the careful operations necessary to yield accurate gravimetric results.

In order to check his working of the gravimetric process, the student should weigh out 2·4 grammes of a steel proved to be free from chromium, and add before dissolving in HCl say exactly 0·1 gramme of pure dry $K_2Cr_2O_7$. The weight of oxide or phosphate obtained should calculate out to 1·475 % of metal. It should also be ascertained that the volumetric method is being carried out under correct conditions by taking 2 grammes of the chromium free drillings, and before dissolving in dilute sulphuric acid, adding from the burette say 25 cc. of the standard bichromate solution. On titrating the excess of ferrous iron left at the end of the operation, exactly 25 cc. of standard solution should remain in the burette.

Gravimetric Estimation of Nickel (Author).

The following method has been worked out in the Laboratory of the Sheffield Technical School, and if the empirical conditions of analysis are strictly followed, gives practically accurate results, as near the truth as can be expected from a process in which the final precipitate is thrown down by a fixed alkaline hydrate.[1]

Re-agents required.

Solution of pure sodic hydrate.—This is freshly made up for each estimation by dissolving in a platinum dish about 10 grammes of pure sodic hydrate (from sodium) in 20 cc. of distilled water.

Saturated solution of sodic acetate.—250 cc. of cold distilled water are saturated with pure re-crystallized sodic acetate, and the solution is filtered from the excess of salt, and is preserved for use in a green glass bottle provided with an india-rubber stopper.

Bromine water.—Made by saturating cold distilled water with pure bromine, and decanting off the red-brown solution from the excess of bromine into a clean stoppered bottle.

The Process.

(Time occupied, about 4 hours.)

Weight taken.—Weigh out 2·4, 1·2, or ·6 grammes of nickel steel drillings into a 20-oz. covered beaker; the

[1] Great care should be exercised to obtain pure sodic hydrate and acetate. If impure a blank estimation containing a small known quantity of a pure nickel salt must be made with Swedish iron, and the weight over theory is deducted from that obtained from the steel. The error is usually due to Al_2O_3.

weight last named is suitable for a steel containing say 6 % of nickel.

Dissolving.—Add in the case of 2·4 grammes of steel 30 cc. of strong hydrochloric acid, and heat the contents of the beaker till the drillings have dissolved, and only a residue of flocks of black carbide of nickel remains. Then quietly boil the liquid till the bulk of the acid has vaporized, and a pasty mass of ferrous chloride has separated.

Diluting, neutralizing, and reducing.—Next add 200 cc. of hot water, rinse the cover and sides of the beaker, and little by little add the solution of sodic hydrate, well stirring the liquid with a glass rod between each addition till the acid is neutralized, and a faint permanent precipitate is produced. Then pour down the rod into the neutralized liquid 25 cc. of strong sulphurous acid solution, cover the beaker, and boil off the SO_2.

First precipitation of the nickel.—Add 15 cc. of 33 % acetic acid solution, and by means of a glass tube inserted under the cover down the lip of the beaker, pass through the boiling fluid a brisk current of washed H_2S generated from a Kipp's apparatus, *well-charged* with FeS and fairly strong hydrochloric acid. Move the cover a little aside, and gradually pour down the side of the beaker 25 cc. of the saturated solution of sodic acetate, previously heated nearly to boiling. Continue to pass the H_2S through the steadily boiling solution for 5 minutes; remove the beaker from the plate, detach the precipitating tube, and allow the black precipitate to settle a little.

Filtering.—By means of the tube guide the solution into a 2¼-in. funnel containing a 110 mm. pure paper. The filtrate, which is conveniently received into a 14-oz. conical beaker, is at first clear and colourless, but soon becomes

brown from atmospheric oxidation. When most of the precipitate is on the filter, wash the tube inside and out, and place it clean end downwards in a filter-drier. Thoroughly rinse out the beaker, washing any easily removed precipitate on to the filter; but it is not necessary to detach any strongly adhering film; the precipitate and paper are washed with hot water, and are then allowed to drain.

Re-dissolving the precipitate.—Carefully detach the paper from the funnel, and place it bodily in the beaker in which the precipitation took place; put on the cover, and add about 35 cc. of strong nitric acid, spec. gravity 1·43. Boil the mass till the filter-paper is decomposed with evolution of deep red-brown fumes, and only suspended fibres remain in the acid. Next cautiously add, about a gramme at a time, well boiling between each addition, pure crystallized chlorate of potash, till the solution becomes *clear from fibres,* and only a globule or two of yellow sulphur remain. The chlorate of potash is best added by drawing the cover of the beaker a little aside, and quickly dropping it into the liquid from a slip of stiff paper; several grammes will be required to completely free the solution from organic matter. Then heat the black end of the precipitation tube in the beaker till free from adhering film, rinse it inside and out, and remove.

Evaporation to low bulk.—The acid solution is now evaporated, at first keeping the cover on the beaker, to a volume of not more than 5 cc., when potassium salts will have crystallized out in some quantity. These are completely taken up by boiling, after diluting with 50 cc. of water.

Neutralizing.—The solution is next treated with pure sodic hydrate till a faint permanent precipitate is ob-

tained, which is re-dissolved in a *few drops* of hydrochloric acid.

Precipitating the iron.—Rinse the cover and sides of the beaker, and add 150 cc. of *cold* water, and 25 cc. of *cold* sodic acetate solution; well stir the liquid with a glass rod, and wash and remove the latter. The *clear* reddish fluid is then gradually heated to boiling, and is boiled for two or three minutes.

Filtering off the iron.—Transfer the solution and precipitate without loss to a 300 cc. flask; dilute to slightly over the mark, well mix, and note the temperature of the solution at a volume of 300 cc., and filter off through a dry filter 250 cc. of the liquid at the same temperature in the manner described on p. 140.

Final precipitation of the nickel.—Transfer the clear greenish solution from the 250 cc. flask to a 20-oz. beaker, and well rinse out the flask. Add 25 cc. of bromine water, and then little by little, with constant stirring, pure sodic hydrate solution, till a black precipitate is thrown down, and the liquid is *distinctly alkaline* when tested with red litmus paper. The contents of the covered beaker are then digested at a temperature just short of boiling till the precipitate has flocked out, leaving the liquid crystal clear.[1]

Filtering.—Collect the quickly filtering black precipitate on a 110 mm. pure paper, and wash it with nearly boiling water till the washings are free from alkali, and no longer turn red litmus paper blue.

Igniting and weighing.—The precipitate is dried as usual, ignited in a tared platinum crucible, and when cold 2 cc. of 1·2 nitric acid are added to the crucible. The contents are then gently evaporated to complete dryness, are again

[1] Sometimes it has a faint pink tinge, due to mere traces of $HMnO_4$.

strongly ignited, and the crucible, after becoming quite cold in the desiccator, is re-weighed. The increase is NiO, containing 78·5 % of metal.

Example of a Determination.

40 lbs. of bar-iron were melted with 20 oz. of cube nickel. The ingot on analysis gave the following result :—

Weight taken 1·2 grammes.

$$
\begin{array}{rr}
\text{Weight of crucible + ppt} = & 27\cdot9382 \\
\text{Weight of crucible} = & 27\cdot9024 \\
\hline
NiO = & \cdot0358 \\
 & 78\cdot5 \\
\hline
 & 1790 \\
 & 2864 \\
 & 2506 \\
\hline
 & 2\cdot81030 \ \% Ni^{1}
\end{array}
$$

Estimation of Nickel in Special Steels.

High silicon steels.—In these the silica is rendered insoluble, and is separated according to directions on p. 172.

Tungsten steels.—This element is removed in the manner described on p. 172.

In both the above cases the filtrates are evaporated to very low bulk, are diluted, neutralized with soda, and the analysis is proceeded with as usual.

Copper steels.—When copper is present a large portion of it will be found with the final nickel precipitate. The latter therefore must not be dried, but is dissolved on the paper in the smallest possible quantity of hot, moderately dilute hydrochloric acid. After well washing the filter, the filtrate is diluted to about 200 cc., and a current of washed H_2S is passed through the liquid for 15 minutes.

[1] Assuming the nickel to have been pure and none to have been lost in melting, 3·03 % Ni should have been present in the steel.

The copper is precipitated as sulphide and is filtered off, the precipitate and paper being well washed with very dilute hydrochloric acid containing some H_2S. The nickel remains in the acid filtrate as chloride; the liquid is nearly neutralized with pure caustic soda, and the nickel is precipitated with bromine and sodic hydrate in the usual manner.

Theory of the Process.

It is necessary to vaporize most of the hydrochloric acid from the preliminary solution to economize the pure soda used for neutralizing. The reduced solution contains ferrous, nickelous, and manganous (and possibly aluminic and chromic) chlorides. On passing H_2S through the solution containing free acetic acid and sodium acetate, the nickel is completely thrown down as black NiS mixed with black FeS and some sulphur. The proportions of the last-named substances are much increased if any ferric chloride was present in the liquid, and also if the air is not as far as possible kept away from the surface of the solution by performing the precipitation whilst the liquid is briskly boiling. The manganese remains in solution as acetate, as do chromium and aluminium if present. If, however, any P_2O_5 is present in the liquid, phosphates of the two metals last named will be found in the nickel precipitate. The combined action of the nitric acid and chlorate of potash completely decomposes the organic matter of the filter-paper. On treating the solution containing the nickel and iron with ammonium acetate in the cold, both metals remain at first in clear solution as acetates, but on heating, the iron (the proportion of the latter carried down as FeS being usually about

equal in weight to the co-precipitated *NiS*) is completely thrown down as basic acetate (possibly mixed with small quantities of chromic and aluminic phosphates) free from nickel. If the precipitation of the ferric acetate is *at once* brought about by adding the ammonium acetate to a *hot* solution, there is danger of a little nickel being carried down with the iron precipitate. The $\frac{5}{6}$ of the filtrate equivalent to 2 grammes, 1 gramme, or $\frac{1}{2}$ gramme of steel, as the case may be, contains greenish, nickelous acetate, which, on treatment with bromine and soda, throws down a black precipitate usually supposed to be the hydrate of nickelic oxide Ni_2O_3. This precipitate has a great advantage over the slimy, apple-green hydrate of nickelous oxide *NiO*, in the fact that it is filtered and washed much more quickly than the latter. With reference to its composition, however, it appears ultimately to consist chiefly of *NiO*. The author has made attempts to estimate the nickel by a volumetric reaction similar to that utilized for the estimation of manganese on p. 86, but the results obtained indicated that the oxygen yielded by the black precipitate was far short of that required for the formula Ni_2O_3; in fact, the oxidation of the ferrous iron was only equivalent to the presence of about 15% of Ni_2O_3, the remainder of the precipitate being evidently *NiO*. The reason for treating the ignited precipitate with nitric acid is to convert any nickel reduced to the metallic state by the action of the carbon of the filter-paper into nitrate. The latter on the second ignition yields *NiO*. Throughout the foregoing analysis it is necessary to employ sodium salts, because nickelous hydrate is soluble in ammonium salts and ammonia.

GRAVIMETRIC ESTIMATION OF ALUMINIUM (Author).

Aluminium steel, in the sense that the material contains a considerable percentage of the somewhat costly metal alloyed with the iron, can hardly be considered as a commercial product, but steels which have been treated to prevent blow-holes with a small percentage of aluminium, and consequently contain a few hundredths of 1 % of that metal, are now of fairly frequent occurrence. The accurate determination of so small a quantity of aluminium associated with such a comparatively enormous mass of iron is a matter requiring considerable care and skill; the chemical reactions of the two metals being so closely analogous. The following process is designed for steels containing not more than 0·1 % of aluminium. It must not be applied without some modification (which will be referred to later on) to steels containing a considerable percentage of *Al;* neither is it suitable for chrome steels.

Re-agents required.

Strong sodic hydrate solution.—This may be prepared as required in a platinum dish; the author, however, prepares and preserves it in a half-pint silver bottle fitted with an india-rubber stopper previously well boiled in caustic soda solution and afterwards in water. In this bottle 100 grammes of pure soda from sodium are dissolved in 100 cc. of distilled water. The re-agent is withdrawn from the bottle by means of a 5 cc. pipette. (*The student must be careful not to suck up the solution into the mouth, it is a most violent corrosive poison.*)

Standard solution of sodium phosphate.—This solution must contain in 1 cc. (measured from a 1 cc. pipette)

enough P_2O_5 to precipitate 0·1 % *Al* in 6 grammes of steel as phosphate. It is made by dissolving 7·87 grammes of crystallized ordinary phosphate of soda (Na_2HPO_4 12 H_2O) in hot water, and diluting the liquid when cold to 100 cc. It should be preserved in a well-stoppered bottle labelled with the strength of the solution.

The Process.

(Time occupied, about 1 day.)

Weight taken.—Weigh out into a 30-oz. registered flask 6 grammes of the steel.

Dissolving.—Add to the drillings 1 cc. of the standard sodium phosphate solution (*this must not be forgotten*) and 50 cc. of strong *HCl* solution. Place a watch-glass on the flask, heat quietly, and finally boil on the hot plate till the drillings have dissolved.

Diluting.—Then dilute with 200 cc. of hot water.

Neutralizing and reducing.—Bring the liquid nearly to boiling, and little by little, and finally drop by drop, constantly shaking the solution round, add dilute ammonia till a slight permanent precipitate is obtained; then add 25 cc. of strong H_2SO_3 solution, and boil till no smell of SO_2 is noticeable.

First precipitation.—Next, all the time keeping the pale-green liquid gently boiling, add slowly 5 cc. of 33 % acetic acid solution, then, a few cc. at a time, 25 cc. of hot ammonium acetate solution, after which briskly boil for 2 or 3 minutes.

First filtration.—Remove the flask from the plate, allow the precipitate to settle somewhat, and then pour through an ashless filter 110 mm. in diameter, contained in a 2¼-in.

ribbed funnel (to which is attached by means of india-rubber tubing the glass loop shown in Fig. 2), as much as possible of the liquid before throwing the precipitate on the filter. The filtrate should be at first quite clear and pale-green in tint, but it soon becomes dark coloured and turbid, a scum also forming on the filter-paper and in the flask. Drain as much as possible of the liquid into the filter, and let it all pass through, the filtrate may then be thrown away. No attempt must be made to wash either flask or precipitate.

First re-dissolving.—Remove the funnel (detach the looped glass), and place it in the neck of the flask in which the precipitation took place. Dissolve the precipitate in boiling hydrochloric acid contained in a beaker, and pour round the edges of the paper by means of a glass rod, using as little acid as possible. Wash the paper alternately with a little hot acid and cold water till free from iron salt; it may then be thrown away. Wash into the flask any splashings on the stem of the funnel, and remove the latter. Boil the solution till the scum on the sides of the flask is dissolved and the liquid a clear yellow.

Repetition of above operations.—Dilute with hot water to 200 cc., bring nearly to boiling, neutralize the dilute ammonia, reduce with sulphurous acid, add 5 cc. of acetic acid solution, and precipitate with ammonium acetate exactly as before. Filter off the precipitate, this time washing out the flask with hot water, slightly wash the precipitate, and allow it to drain. Place the funnel inside a 20-oz. beaker on a glass hanger, and dissolve up the precipitate in hydrochloric acid boiled in the flask in which the precipitation took place. Well rinse out the flask, and thoroughly wash the filter-paper as before, then remove the funnel and hanger.

Evaporating nearly to dryness.—To the contents of the beaker add 2 *drops* of strong nitric acid (to fully peroxidize the iron), put on the cover, and boil down to low bulk, then, removing the cover, *very gently evaporate almost to dryness.*

Precipitating the iron.—Take up the moist crystals of ferric chloride in 10 cc. of water, and wash every drop into a deep 3-in. platinum dish: the volume of the liquid should be about 25 cc. Next add 5 cc. of the strong solution of sodic hydrate, thoroughly but quickly stir the solution with a glass rod (of course well washing the latter), place the dish on a pipe-stem triangle on the hot plate, cover it with a 4-in. clock-glass, and maintain at a gentle boil for 15 minutes. Remove and allow to cool.

Filtering off the sodic aluminate.—Pinch up the edges of the platinum dish so as to form a temporary spout, and cautiously pour the solution and precipitate into a 60 cc. flask, into which every trace of solution must be washed out of the dish with cold water; dilute exactly to the mark, and thoroughly mix the contents of the flask, then, through a dry double filter contained in a 2-in. funnel, filter off 50 cc. of the clear liquid.

Precipitation of the aluminium.—Transfer the liquid from the 50 cc. flask into a 20-oz. beaker containing 25 cc. of strong HCl, add 10 cc. of a 10 % solution of sodium phosphate, bring the liquid to a gentle boil, and then little by little add (down the lip of the beaker, the cover being kept on) dilute ammonia solution till the acid is neutralized, a white gelatinous precipitate thrown down, and a *faint* smell of ammonia is perceptible. Digest the contents of the beaker just short of boiling till the precipitate has gathered into flocks and the liquid is clear. Remove the beaker from the plate and allow the precipitate to settle.

Filtering.—Pass as much as possible of the clear liquid through a 110 mm. paper contained in a 2-in. funnel, then, with the aid of a policeman and the wash-bottle jet, bring every particle of the precipitate on to the paper, and *thoroughly* wash the filter with almost boiling water till the washings fail to produce the slightest opalescence when added to a dilute solution of silver nitrate contained in a test tube.

When the precipitate has thoroughly drained, dry it in the usual manner, strongly ignite in a tared platinum crucible, and weigh the white residue when cold in the usual manner. Its formula is approximately $AlPO_4$, containing 22·2 % of metallic aluminium. Calculate the percentage on 5 grammes of steel.

Blank determination.—It is highly advisable in this process to make on 6 grammes of a steel free from aluminium a determination of the extraneous metal present in the re-agents used or possibly taken up during the analysis; the weight obtained is of course deducted from that of the precipitate obtained from the aluminium steel.

Example of Calculation.

Feb 9, 1891.

Crucible cast steel ingot No. 87 (to which was added 0·1 % *Al*).

Weight of steel taken, 6 grammes.

Crucible + ppt = 28·6236
Weight of crucible = 28·6097
·0139
Less blank = ·0027
·0112 gramme $AlPO_4$
22·2
224
224
224
5)·24864
·0497 say 0·05 % *Al*.

Cases of Special Steels.

High silicon.—If a large percentage of silicon is present, it is best before proceeding with the analysis to evaporate the hydrochloric acid solution of the steel to dryness; take up in HCl and filter off the silica, which would otherwise obscure the correct neutralization of the solution. When reducing the filtrate, it is advisable to use 50 instead of 25 cc. of SO_2 solution, because more ferric chloride will be present.

Tungsten.—In the case of tungsten steels, it is necessary to add to the preliminary hydrochloric acid solution 10 cc. of strong nitric acid, evaporate to dryness, bake well, take up in HCl, and filter off the tungstic acid. This is most speedily and conveniently accomplished by taking originally 7·2 grammes of steel, making up the solution containing the tungsten precipitate to 90 cc., and filtering off 75 cc. which will contain the aluminium in 6 grammes of steel. As the iron in solution will be totally in the ferric condition, at least 100 cc. of sulphurous acid will be required to perfectly reduce the neutralized yellow ferric chloride to pale-green ferrous chloride.

Theory of the Process.

After the neutralization there is present a mixture of ferrous, manganous, aluminic, and ferric chloride; the last-named (formed by the action of the air, as described on p. 69) must be again reduced to the ferrous state. This is effected by the reaction given on p. 120.

On the removal of the free mineral acids by the addition of ammonium acetate (see p. 121), the aluminium is

thrown down as the normal phosphate $AlPO_4$, which is insoluble in dilute acetic acid. The phosphoric acid present (as phosphate of soda and a little phosphate of iron from the steel) in excess of the amount required by the aluminium, throws down some ferrous phosphate $Fe_3(PO_4)_2$, and the amount of iron in the precipitate is also increased by the atmospheric oxidation of the ferrous acetate, which forms a scum of basic *ferric* acetate insoluble in acetic acid. On the second precipitation, however, the solution of iron being comparatively very dilute, the phosphate of alumina has associated with it a much smaller quantity of iron. This, however, must be totally separated by boiling the concentrated and nearly neutral solution of the two metals with an excess of caustic soda. Ferric hydrate is precipitated, and sodic aluminate remains in solution, thus—

$$FePO_4 + 3\ NaHO = Fe(HO)_3 + Na_3PO_4$$

$$2\ AlPO_4 + 8\ NaHO = (NaAl)_2O_4 + 2\ Na_3PO_4 + 4\ H_2O$$

The solution of aluminate of soda in excess of sodic hydrate gives no precipitate with ammonia till it has been decomposed with excess of hydrochloric acid, thus—

$$(NaAl)_2O_4 + 8\ HCl = 2\ NaCl + 2\ AlCl_3 + 4\ H_3O$$

The aluminic chloride is at once converted by the sodium phosphate present into aluminic phosphate (which remains dissolved in the excess of acid) thus—

$$AlCl_3 + Na_3PO_4 = 3\ NaCl + AlPO_4$$

When the excess of hydrochloric acid is neutralized, forming $AmCl$, and a faint excess of ammonia substituted, the normal phosphate of alumina is precipitated by the excess of phosphoric acid present; in the absence of sufficient phosphoric acid a basic phosphate $Al_4P_6O_{19}$ similar to that of chromium is thrown down, but it is less certain in composition than the salt of the metal last named.

The success of the foregoing method depends in a

great measure upon having the phosphoric acid present only *slightly* in excess of the amount required theoretically to precipitate the aluminium. If a large excess of P_2O_5 is in the solution, so much ferrous phosphate is carried down with the aluminium salt as to render the process almost impracticable. The method can of course be applied to steels containing high percentage of *Al* (see analysis of ferro-aluminium, p. 217), if only the percentage of the latter is roughly known. In a steel works the analyst should have no difficulty in ascertaining the maximum percentage possible, and a quantity of sodium phosphate sufficient to precipitate that percentage should be added, calculated on the much smaller weight of steel employed. Unfortunately, however, some works managers who are unacquainted with analytical chemistry, are possessed with the curious idea that the best way to get accurate reports is to keep the chemist as much as possible in the dark concerning the calculated composition of the steels sent up to the laboratory.

The principle of taking $\frac{5}{6}$ths of the liquid in order to avoid a tedious and in this case somewhat dangerous washing of the precipitate, has already been explained with reference to the estimation of manganese on p. 82. If the aluminium in 6 grammes of steel is contained in a volume of liquid measuring 90 cc., then the metal in 5 grammes of steel will be contained in $\frac{5}{6}$ of $90 = 75$ cc.

Volumetric Estimation of Copper (Author).

(Time occupied, about 3 hours.)

Re-agents required.

Standard solution of "Hypo."—Powder and dry (by pressing the spread-out salt between filter-paper) a few grammes of moist crystals of pure sodium hyposulphite (thiosulphate) $Na_2S_2O_3$, 5 H_2O. Weigh out 3·938 grammes of the salt into a litre flask, and dissolve in a few hundred cc. of cold distilled water, dilute to the mark, and thoroughly mix the liquid. The standard solution thus prepared should be preserved in the dark, otherwise it is liable to decompose with precipitation of sulphur. It is advisable to frequently make up a new solution.

Starch solution.—Make about one gramme of wheat or arrowroot starch into a thin paste with 5 cc. of water. Boil in a 20-oz. beaker about 100 cc. of distilled water. Remove it from the plate, and pour into the hot water the 5 cc. of cold starch cream. Well mix the emulsion by shaking the beaker round, and *filter* off a portion of the clear liquid for use. This re-agent must be freshly made for each set of estimations.

Potassic iodide free from iodate.—To prove the freedom of the iodide (KI) from iodate (KIO_3), dissolve a crystal in a test tube containing 10 cc. of water; add 1 cc. of starch liquor, and then a few drops of acetic acid. No blue coloration should be developed.

Solution of sodium carbonate.—Saturate 250 cc. of cold water with pure Na_2CO_3, filter for use, and store in a green glass bottle fitted with an india-rubber stopper.

Electrotype copper.—Polish some electro-deposited copper-foil with fine emery-cloth, and cut it up with a pair of scissors into conveniently small pieces.

Standardizing the "Hypo" Solution.

Standard copper solution.—Weigh out exactly 5 grammes of the pure copper into a 20-oz. beaker, put on the cover, and add cautiously in three portions 30 cc. of nitric acid, sp. gr. 1·20. Heat gently to boiling on the hot plate, and when the metal has all dissolved remove the cover, rinsing any splashings on it and the sides of the beaker into the solution. Next very quietly evaporate to low bulk till cupric nitrate begins to crystallize out. Add 50 cc. of water, and dissolve up every particle of the separated salt, and then without loss transfer the blue liquid to a litre flask. When cold dilute to the mark, and thoroughly mix the solution. Keep in a stoppered bottle labelled—"$Cu(NO_3)_2$. 10 cc. = 0·05 gramme of metallic copper."

Titrating.—From a pipette deliver exactly 10 cc. of the standard *Cu* solution into a 20-oz. beaker. Put on the cover, and little by little, constantly shaking round the beaker, add down the lip the strong solution of sodium carbonate till no further evolution of CO_2 is noticed, and the copper is all thrown down as a pale-blue precipitate. Every trace of this is next dissolved up by gently boiling with a *slight* excess of dilute acetic acid. Thoroughly cool the liquid, and add about 2 grammes of potassium iodide crystals, and shake round the beaker till they have dissolved. Fill up a 50 cc. burette with the "hypo" solution, and set the meniscus at zero. Then run the

thiosulphate into the copper solution till the brown tint of the dissolved iodine has become much fainter; this should happen when about 45 cc. have been run in. Then add 2 cc. of clear strong starch liquor, when a dark-blue colour will be produced. Cautiously continue the addition of the "hypo" half a cc., and finally a few drops at a time, continually shaking round the contents of the beaker till the blue colour has been totally discharged. It should not reappear on the solution standing for a few minutes. The end of the reaction requires a little experience for its correct determination. It is best decided by noting when a few drops of liquid from the burette no longer produce a lighter patch or streaks in the surrounding liquid, which has for a background a precipitate of yellowish-white cuprous iodide CuI. If the solution of "hypo" is of correct strength, just 50 cc. should be required to discharge the colour of the iodide of starch. If the standard liquid is not exactly right, the student should have no difficulty in correcting it either for strength or weakness after referring to the examples given for adjusting the standard solution of $K_2Cr_2O_7$ on p. 89. The above titration must never be made when fumes of bromine vapour or of aqua regia (chlorine) are present in the air of the laboratory, because these elements at once liberate free iodine from a solution of KI, and thus render the accurate determination of the final point almost impossible. Nitrous acid and the nitrites must also be avoided in the re-agents used.

The Process for Steel.

Weight taken.—Weigh out 10 grammes of drillings into a covered 20-oz. beaker.

Dissolving.—Add 60 cc. of strong hydrochloric acid.

When the reaction has somewhat subsided, quietly heat on the plate till the steel has dissolved, and then boil the solution till most of the acid has been driven off, and crystals of ferrous chloride have commenced to separate, making the solution thick. Then cautiously add down the lip of the beaker 300 cc. of warm water, and heat if necessary till the whole of the separated ferrous chloride has re-dissolved; then remove from the plate. During this dissolution the cover should not be taken off.

Precipitating the copper.—Next, by means of a glass tube about 9 in. long (inserted under the cover down the lip of the beaker), pass through the solution for ten minutes a brisk current of washed H_2S gas (from a Kipp's apparatus well charged with FeS and slightly diluted HCl solution), when the dark precipitate should have flocked out, leaving a clear pale-green liquid somewhat opalescent with finely-divided sulphur. Detach the glass tube (from the india-rubber tubing of the washing cylinder) and leave it in the beaker.

Filtering.—When the precipitate has somewhat settled, guide the clear liquid by means of the tube into a 110 mm. pure filter contained in a 2¼-in. ribbed funnel supported in a conical beaker. When most of the filtrate has passed through the filter, throw on the dark CuS (mixed with sulphur, FeS, etc.), and rinse the beaker and tube free from every trace of iron solution, but do not attempt to detach any strongly adhering precipitate from either. Leave the tube in the beaker, and well wash the paper and sulphide of copper till free from iron salt with cold water containing some H_2S and 5 cc. of strong HCl solution per 100 of water. Finally wash once with cold water.

Dissolving up the precipitate.—Wash the funnel free from any splashings of ferrous chloride solution, and support it

inside the beaker in which the precipitation took place on a glass hanger. *Cautiously* treat the filter with hot 1·20 nitric acid to dissolve up the precipitate, using as little acid as possible. It almost invariably happens that some crusts of sulphur, black with intermixed sulphides, remain insoluble. These, after the filter has been well washed with hot water, must be added to the copper solution by spreading out the paper on a beaker cover, and detaching them with the aid of a fine jet of water.

Separating co-precipitated iron.—Boil the nitric acid solution in a covered beaker till the crusts of sulphur are yellow; then add cautiously dilute ammonia till the acid is neutralized, and the deep blue liquid has a distinct smell of the alkali. Boil for two or three minutes, and filter off the copper solution into a clean 20-oz. beaker, collecting the precipitated $Fe_2(HO)_6$, SiO_2, sulphur, etc. in a 2-in. funnel containing a 90 mm. pure paper. The latter must be well washed with hot water, using, however, as little as possible.

Conversion of the copper into acetate.—To the covered beaker containing the ammonio-copper solution, add a few drops of strong nitric acid, till the deep blue of the liquid is changed to a pale greenish-blue tint, then boil down to about 10 cc. Next add, a few drops at a time, the strong solution of sodium carbonate till the deep azure blue colour is permanently reproduced. Then add, drop by drop, acetic acid till it is again discharged, being replaced by a much paler blue. Remove the beaker from the plate, and place it in a bath of cold water till the contents are cool.

Titrating the copper.—Next add to the cold liquid, the bulk of which should not exceed 25 cc., about 2 grammes of potassic iodide and titrate with hypo and starch liquor,

exactly in the manner already described for checking the standard, only of course in the present case, the amount of copper being unknown, great care must be exercised in watching the yellowness of the solution so as not to overshoot the mark before adding the starch. The latter could be put into the solution immediately after the dissolution of the iodide, but would then precipitate the iodine in flocks of iodide of starch, which are not so readily acted upon by the thiosulphate as when in solution, which condition is ensured when only traces of iodine are left at the time the starch is added.

Each cc. of hypo used equals 0·01 % *Cu* on 10 grammes of steel. Thus, if the reaction were finished when 9 cc. had been run in, the copper present = 0·09 %; if 27 cc. were required the copper = 0·27 %. If the whole 50 cc. failed to discharge the colour of the starch solution, more than 0·5 % *Cu* was present in the steel. Such, however, will never be the case in ordinary steels. When an experimental steel containing over 0·5 but under 1 % of copper has to be dealt with, take for the assay only 5 grammes of steel, when each cc. required will equal 0·02 or 50 cc. = 1 % *Cu*. It is also easy to adjust the strength of the thiosulphate solution to take any percentage of copper; the basis of the above process having been originally devised for the analysis of copper alloys by Mr. E. O. Brown.

Estimation of Copper in Tungsten Steel.

In the case of tungsten steel, proceed to obtain the acid ferrous solution (from which to precipitate the *CuS*) free from this element in the manner described in the article on the estimation of aluminium on p. 172.

Theoretical Considerations.

The reactions taking place in titrating the standard copper solution will be first considered. On adding the Na_2CO_3 solution to that containing the nitrate of copper in which is a little free nitric acid, CO_2 is evolved, and sodium nitrate $NaNO_3$ is formed as the result of the neutralization of the acid. The excess of sodium carbonate then precipitates basic carbonate of copper $(CuCO_3, Cu(HO)_2)$. On the addition of an excess of acetic acid, the surplus sodium carbonate is converted into sodium acetate $Na(C_2H_3O_2)$, and the copper precipitate is dissolved up, forming cupric acetate $Cu(C_2H_3O_2)_2$ with evolution of CO_2.

The reactions occurring in the case of steel will now be dealt with. On dissolving up the drillings, the finely-divided copper diffused throughout the mass of the iron is attacked by the hydrochloric acid with formation of cupric chloride, $CuCl_2$.

The copper in the hydrochloric acid solution is separated from the soluble iron by the H_2S as a dark-brown sulphide insoluble in dilute acids, thus—

$$CuCl_2 + H_2S = CuS + 2\ HCl$$

By an analogous reaction the sulphide of copper is contaminated with a small quantity of co-precipitated FeS. On dissolving up the sulphides in nitric acid, they are oxidized by a complex reaction to cupric sulphate $CuSO_4$ and ferric sulphate $Fe_2(SO_4)_3$.

On adding an excess of ammonia to the nitric acid solution, the acid is neutralized with formation of ammonic nitrate $AmNO_3$, ferric hydrate $Fe_2(HO)_6$ is precipitated, whilst the copper remains dissolved in the excess of ammonia as a compound possessing the formula $(CuSO_4,$

4 NH_3). On acidifying the liquid with nitric acid, the last-named substance is decomposed into a mixture of copper sulphate and ammonium nitrate, but it is again formed on the addition of excess of sodium carbonate, owing to the liberation of free ammonia from the ammonium nitrate, thus—

$$Na_2CO_3+2\ AmNO_3=2\ NaNO_3+CO_2+2\ NH_3+H_2O$$

On acidulating with acetic acid, the ammonio-cupric compound is again decomposed with formation of cupric acetate and ammonium acetate and sulphate, thus—

$$(CuSO_4,4\,NH_3)+4\,C_2H_4O_2=Am_2SO_4+2Am(C_2H_3O_2)+Cu(C_2H_3O_2)_2$$

The following reactions are common to the cases of the standard and the steel. On the addition of potassium iodide to the acetic acid solution of cupric acetate, the following changes take place—

$$Cu(C_2H_3O_2)_2+2\ KI=I+CuI^1+2\ K(C_2H_3O_2)$$

Cupric acetate and potassic iodide yield free iodine (which remains dissolved in the excess of KI added), cuprous iodide (a soiled white precipitate), and soluble acetate of potassium.

On running in the solution of thiosulphate to that containing the iodine, the following reaction ensues—

$$Na_2S_2O_3+I=NaS_2O_3{}^1+NaI$$

Sodium thiosulphate and iodine yield sodium tetrathionate and sodium iodide.

The starch indicator owes its colour to the formation of blue iodide of starch, a compound readily robbed of its iodine by hypo. It therefore only retains its tint as long as any *free* iodine is present, and consequently as soon as

[1] Theoretically the equations require doubling, but for simplicity are expressed in their lowest terms; the actual compounds are Cu_2I_2 and $Na_2S_4O_6$.

the latter is converted into the sodium salt the colour disappears.

On studying the above reactions, it will be seen that, firstly, each atom of copper weighing 63 liberates its equivalent of one atom of iodine, weighing 127; and secondly, that each molecule of thiosulphate, weighing 248,[1] converts one atom of iodine into iodide of sodium: therefore 248 parts of the hydrated thiosulphate correspond to 63[2] parts of metallic copper. But in 50 cc. of the standard solution we have 0·1969 gramme $\left(\frac{3 \cdot 938}{20}\right)$ of hypo.

$$\text{Then if } 248 \text{ parts of hypo} = 63 \text{ parts } Cu$$

$$0 \cdot 1969 \quad ,, \quad ,, \quad = x \quad ,,$$

$$\frac{0 \cdot 1969 \times 63}{248} = 0 \cdot 05 \text{ gramme } Cu$$

Or 0·5 cc. = 0·0005 gramme Cu = 0·01 % of 10 grammes.

It is of great importance to separate the small quantity of iron precipitated with the copper, because ferric salts liberate iodine from potassic iodide, and their presence would therefore cause the result to come out higher than the truth.

In the preliminary solution of the steel the cover should not be removed from the beaker, so as to prevent as far as possible atmospheric oxidation of $FeCl_2$ to $FeCl_3$ (see p. 69). If much of the latter salt be present, a large quantity of sulphur is thrown down with the CuS by the reaction formulated in the following equation—

$$2\ FeCl_3 + H_2S = 2\ FeCl_2 + 2\ HCl + S$$

[1] The original salt contained five molecules of water, weighing 90.

[2] The atomic weights have been taken in round numbers, which in the present case are sufficiently accurate.

DETERMINATION OF IRON (Penny).

Re-agents required.

Standard solution of $K_2Cr_2O_7$.—Weigh out into a clean, dry 10-oz. beaker exactly 4·383 grammes of pure, dry, selected crystals of potassium bichromate. Dissolve the salt in about 250 cc. of hot water; when cold, transfer the solution to a litre flask, thoroughly washing out the beaker, make up the liquid to the mark, and thoroughly mix the solution by repeatedly inverting the stoppered flask. Keep in a well-stoppered bottle labelled—"$K_2Cr_2O_7$ 1 cc. = 1 % *Fe* on 0·5 gramme." Standardize and adjust the solution in accordance with the directions given on pp. 86, 87. 0·501 gramme of the standard iron should require exactly 100 cc. of bichromate.

The Process.

(Time occupied, about 1 hour.)

Weight taken.—Weigh out into a clean, dry 10-oz. flask exactly 0·5 gramme of the steel drillings.

Dissolving.—Add to the metal 25 cc. strong HCl mixed with 15 cc. of water, cover the flask with a watch-glass, and gently heat the liquid to boiling till the iron has dissolved, and only some black flocks of carbonaceous matter remain.

Oxidizing the organic matter.—Rinse the watch-glass with a little hot water, and add in three portions about 3 grammes of chlorate of potash crystals, boiling the liquid between each addition, and especially after adding the last gramme of salt.

Neutralizing.—The acid solution of perchloride of iron is next neutralized with dilute ammonia (half 880, half water) added little by little, the liquid being well shaken between each addition, till a slight permanent precipitate is obtained.

Reducing.—Pour down the sides of the flask about 25 cc. of a saturated solution of sulphurous acid, and briskly boil the liquid till every trace of SO_2 has been expelled, and the solution is of a faint, sea-green colour, *quite free from any yellow tinge.*

Titrating.—Add to the solution 10 cc. of dilute sulphuric acid: the iron is then determined by the standard solution of $K_2Cr\,O_7$, with a dilute solution of potassic ferricyanide as indicator, in the manner fully described on pp. 86, 87. Each cc. required = 1 % *Fe.* Example—

0·5 gramme of a Bessemer spring steel required 98·2 cc. of the standard liquid: therefore the iron equalled 98·2 %.

Theoretical Considerations.

These have been already dealt with on p. 88; the only point requiring mention is the fact, that in steel containing any appreciable percentage of carbon it would not be safe to dissolve the drillings in dilute sulphuric acid and directly titrate the solution, because the solid, residual carbonaceous matter which has escaped evolution in the form of hydrocarbons has a slight but distinct reducing action upon the bichromate solution, and would therefore cause the result registered to be somewhat high. The organic matter is decomposed by the mixture of chlorine and chlorine peroxide evolved from the chlorate of potash and HCl; but at the same time, the iron is oxidized to the

ferric state, hence the necessity for reducing the nearly neutral liquid with sulphurous acid to the ferrous state (see p. 120). It is not often necessary to directly determine the iron in steel, the metal being usually taken by difference. In certain cases, however, it may be important to directly check the percentage present when making a complete analysis, in order to ensure that no appreciable percentage of any unestimated element has been overlooked.

In estimating iron it is important to bear in mind the fact, that in solutions of perchloride, from which a violent evolution of gas is proceeding, loss of iron may possibly occur during brisk boiling, on account of the volatilization of some ferric chloride with the gas.

ANALYSIS OF PIG-IRON.

Sampling.

Grey irons.—In these the pigs should be broken, and the drillings taken from different parts of the fracture; the danger of getting into the sample sand from the outside of the pig is thus reduced to a minimum.

Mottled and white irons.—These may either be drilled at a slow speed, with a drill made from high quality water-hardening tungsten steel, quenched out at a moderate red heat, or small pieces of the sample may be crushed in the steel mortar, and passed through a sieve of sixty meshes to the inch.

Estimation of Carbon.

Total carbon.—This is determined working on 1 gramme of the sample, exactly as described for steel on p. 29, but the temperature of the combustion should be as high as possible, to ensure burning off every particle of the graphite.

Graphitic carbon.—This is determined on 1 to 3 grammes of the sample, in the manner described for steel on p. 54; the weight 3 grammes has reference to faintly mottled white irons. In highly silicious irons, in which the silica is not completely soluble in dilute nitric acid, it is necessary to make the preliminary solution in hydrochloric acid evaporate to dryness, take up in hydrochloric acid, and collect the total residue on the asbestos plug. The latter is washed free from iron with hydrochloric acid and water, and is then treated with moderately strong caustic potash solution to dissolve up most of the silica. The residual graphite is then washed with hydrochloric acid and water till free from potash. The foregoing procedure is necessary, because gelatinous silica, as separated from nitric acid solution, would clog up the filter to such an extent that the filtration might occupy several hours. The result may be a little high owing to the presence with the graphite of traces of unevolved combined carbon.

Combined carbon.—This may be estimated by colour in the manner described for graphitic steels on p. 52. It is, however, most accurately measured by deducting the percentage of graphite by combustion from that of the total carbon.

Example of Determinations.

Sample of Carnforth No. 1 Bessemer hematite iron.

Total Carbon—

Weight taken, 1 gramme.

Weight of absorption tubes before combustion.

$$\begin{aligned} KHo &= 32{\cdot}3964 \\ CaCl_2 &= \underline{57{\cdot}6349} \\ & \ 90{\cdot}0313 \end{aligned}$$

Weight of absorption tubes after combustion.

$$\begin{aligned} KHo &= 32{\cdot}5233 \\ CaCl_2 &= \underline{57{\cdot}6532} \\ & \ 90{\cdot}1765 \\ & \ \underline{90{\cdot}0313} \\ & \ \ \ {\cdot}1452 \text{ gramme } CO_2. \end{aligned}$$

$$\frac{{\cdot}1452 \times 27{\cdot}27}{1} = 3{\cdot}960\ \%\ \text{Carbon.}$$

Graphite—

Weight taken 1 gramme.

Weight of absorption tubes before combustion.

$$\begin{aligned} KHo &= 32{\cdot}5261 \\ CaCl_2 &= \underline{57{\cdot}6546} \\ & \ 90{\cdot}1807 \end{aligned}$$

Weight of absorption tubes after combustion.

$$\begin{aligned} KHo &= 32{\cdot}6265 \\ CaCl_2 &= \underline{57{\cdot}6813} \\ & \ 90{\cdot}3078 \\ & \ \underline{90{\cdot}1807} \\ & \ \ \ {\cdot}1271 \text{ gramme } CO_2. \end{aligned}$$

$$\frac{{\cdot}1271 \times 27{\cdot}27}{1} = 3{\cdot}466\ \%\ \text{Graphite.}$$

$$\left.\begin{aligned} \text{Total Carbon} &= 3{\cdot}960 \\ \text{Graphite} &= 3{\cdot}466 \\ \text{Combined Carbon} &= \underline{0{\cdot}494} \end{aligned}\right\}\ \%$$

The estimation of the remaining elements found in pig-irons will be dealt with under separate headings, having reference respectively to the cases of non-titanic and titanic metals.

Analysis of Non-Titanic Irons.

Determination of Silicon.

This is carried out much in the same manner as that described for steel on p. 66, but, as a rule, only 1 gramme need be taken for analysis.

Boiling the insoluble residue with aqua regia.—After taking up the soluble portion of the cake resulting from the evaporation of the original hydrochloric acid solution to dryness in 50 cc. of strong HCl, 10 cc. of strong nitric acid are also added, and the liquid is boiled down to 25 cc. before diluting for filtration. This precaution is taken to decompose and render soluble some compound of iron which, particularly in the case of phosphoric irons, is apt to obstinately attach itself to the graphite and silica, the consequence being that the final residue is impure, and red with oxide of iron after ignition.

Washing.—The washing of the residue also must be very thorough, the silica and graphite on the filter being repeatedly treated alternately with fairly strong, hot hydrochloric acid and cold water till every trace of iron is removed.

Igniting.—The ignition in the case of graphitic iron usually occupies at least 20 minutes in a hot muffle before the last traces of graphite are burnt off. The final residue should be snow-white, and quite free from grey patches or any red tinge.

Determination of Manganese.

This is estimated by the ammonium acetate process in the manner described for silicious steels on p. 83.

Estimation of Sulphur.

This is determined by the aqua regia process, exactly as described for steel on p. 96.

Determination of Phosphorus.

This point requires from the analyst careful consideration as to the weight of metal to be employed for the analysis, because, although 0·1 % phosphorus is a somewhat high percentage to occur in steel, in the case of pig-iron as much as 4 % of the element may be present in irons to be converted into steel by the basic process. The author is of opinion, that when the metalloid is to be weighed as ammonio-phospho-molybdate, a quantity of drillings yielding not more than about 0·3 gramme of precipitate should be weighed out, otherwise the yellow compound may not be strictly to formula. The following table will form a rough guide as to the weight of metal conveniently taken for every class of pig-iron, from Swedish pigs smelted from Dannemora magnetite to the most impure iron reduced from the deposits of brown hematite occurring in North Lincolnshire and Northamptonshire.

Approximate % Phosphorus in Iron.	Weight taken for analysis, grammes. Process.		Approximate weight of precipitate obtained. Process.	
	Molybdate.	Combined.	Molybdate.	Combined.
4·00	—	0·25	—	0·032
2·00	0·20	0·50	0·31	0·032
1·00	0·50	1·00	0·31	0·032
0·50	1·00	2·00	0·31	0·032
0·25	2·00	4·00	0·31	0·032
0·10	3·00	6·00	0·18	0·021
0·05	4·00	8·00	0·12	0·014
0·02	5·00	10·00	0·06	0·007

In chemical analysis it should always be borne in mind, that although, *cæteris paribus*, a heavy precipitate reduces the errors of analysis, there are often other considerations to take into account, such as the bulk of the precipitate to be dealt with with reference to convenience as to filtration, thorough washing, ignition, etc. These considerations are important in the present case in connection with the slimy precipitate obtained in the preliminary stage of the combined process (see p. 119), and the ignition of the magnesium pyrophosphate residue, which in large masses is apt to absorb and obstinately retain carbon from the filter-paper. For these reasons it is not advisable to take too great a weight for analysis when dealing with phosphoric pig-iron.

The Processes.

These differ little from those described for the analysis of steel by the long molybdate and combined methods respectively dealt with on pp. 123, 125. It is, however, absolutely necessary, after dissolving up the dry oxide of iron in hydrochloric acid, to again evaporate to dryness, and take up in hydrochloric acid, thus rendering the silica insoluble before diluting the liquid and filtering off the silica and graphite, otherwise the gelatinous silica will seriously clog the filtration of the solution ultimately to be neutralized and reduced in the preliminary process described on p. 118, in which it is of course necessary to add sufficient ferric chloride to precipitate the whole of the phosphoric acid as ferric phosphate, together with some basic peracetate of iron.

Estimation of Phosphorus in Chrome pig-irons.

In the case of chrome pigs the preliminary solution of the iron should be made in aqua regia, because nitric acid leaves a large insoluble metallic residue possibly containing phosphorus. There is usually also some insoluble metallic residue after the evaporation with aqua regia, but it is, as a rule, free from phosphorus.

Estimation of Chromium.

Sampling.—The chromium in specially smelted chrome pig-iron usually occurs alloyed in proportions of from 6 to 12 %. These irons are generally white, and perfectly clean-broken fragments from the pigs must be crushed and passed through a sieve of 90 meshes to the inch before using for analysis.

Method of estimation.—If the iron is low in phosphorus the chromium is best determined by the gravimetric hydrate method described for steel on p. 138. If, however, the pig is phosphoric, the chromium must be estimated as phosphate by the process given on p. 145.

Estimation of Copper.

Copper is determined by the volumetric process described for tungsten steels on p. 180.

Determination of Arsenic.

Weight taken, etc.—Dissolve 6 grammes of the pig-iron in 1·2 nitric acid, and evaporate to dryness in the manner described for steels on p. 131.

Re-dissolving.—When cool, break up the dry cake and transfer to the 300 cc. flask A, Fig. 15 ; cover the beaker, and gently digest the adhering oxide of iron with about 20 cc. strong HCl till the beaker is clean. Pour the yellow liquid into the flask, and rinse out the beaker with

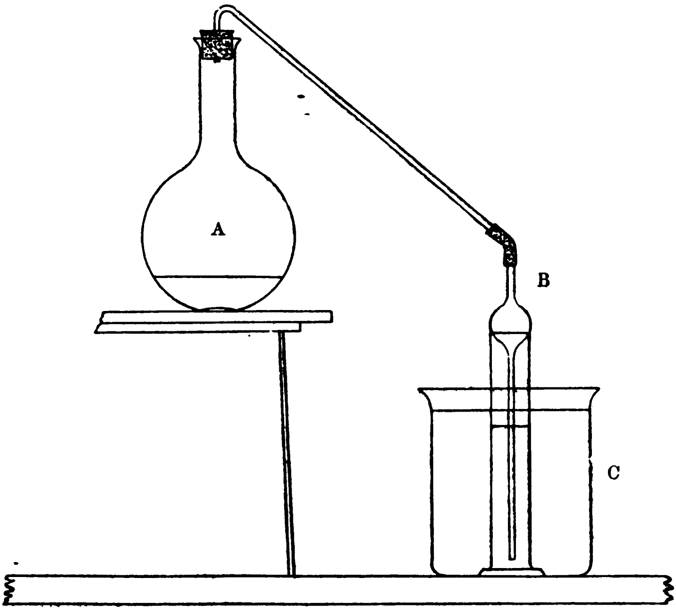


FIG. 15.

additional quantities of strong HCl till free from iron, and the total volume in the flask equals about 60 cc.; the india-rubber stopper carrying the bend is then inserted, and the latter is attached to the bulb-tube B, resting in the 100 cc. measure containing 50 cc. of distilled water, and standing in the beaker of cold water, C. The oxide is

dissolved up, and the acid distilled off till the solution in the flask becomes viscid. The condensing apparatus is then detached, and the flask removed from the plate. Pour the contents of the measure into the flask, well washing the latter and the condensing tubes till the total solution measures about 250 cc.; cool, make up to the mark, thoroughly mix, allow the silica and graphite to settle somewhat, and filter off 250 cc. of the clear liquid, corresponding to 5 grammes of iron; avoid as far as possible throwing the gelatinous silica on the filter, as it is very liable to clog the paper.

Remaining operations.—The liquid is transferred without loss to a 30-oz. registered flask, is neutralized, reduced, the arsenic is precipitated to sulphide, and estimated in the manner already described for steels on p. 129.

Theoretical Considerations.

The above special operation has for its object the separation of most of the silica, which occurs on distillation to low bulk. If the silica remaining in solution on merely gently dissolving up the cake were not rendered insoluble, it would interfere with the subsequent operations, as much of it would be precipitated with the As_2S_3. The distillate is condensed to prevent a loss of arsenic as chloride, and the fractional filtration saves a serious loss of time.

ANALYSIS OF TITANIC PIG-IRONS.

Estimation of Silicon.

In irons containing titanium, some TiO_2 is usually found with the ignited silica. This impurity must be separated

by thoroughly fusing the residue in a platinum crucible with a few grammes of perfectly pure acid potassium sulphate. The fused mass is extracted by gently warming it with moderately strong hydrochloric acid, when the sulphate of titanium passes into solution. The purified, insoluble silica is filtered off, thoroughly washed with hot dilute hydrochloric acid and nearly boiling water, till the washings develop no opalescence when dropped into a dilute solution of barium chloride; the silica is then dried, ignited, and weighed in a covered crucible as usual.

Estimation of Titanium.

(Time occupied, about 2 days.)

An exact method of estimating titanium remains to be discovered; the following process yields only approximate figures. In working it out the author has utilized valuable information given in the researches of Messrs. Riley and Blair on this matter.

The Process.

Weight taken.—Weigh out into a 20-oz. covered beaker 5 grammes of the iron in drillings or powder. *In the cases of hematite, Swedish, or other non-phosphoric irons, add to the drillings about ½ gramme of ammonium phosphate crystals.*

Dissolving.—Add 60 cc. of 1·2 nitric acid, and boil and evaporate to dryness as for the estimation of phosphorus. Take up the dry mass with hydrochloric acid, and again evaporate to dryness as usual.

Collecting the insoluble residue.—The insoluble matter consisting of silica, graphite, and phospho-titanite of iron is collected on a 110 mm. pure paper, and is washed with hot HCl and cold water till free from soluble iron salts. The filtrate is free from titanium.

Fusing the residue with K_2CO_3.—The filter and its contents are dried and ignited in a 3-in. platinum dish, the reddish-yellow residue is intimately mixed with about 10 grammes of pure potassium carbonate, and the mass is fused in a covered dish over a gas blow-pipe till its contents are quite liquid, which condition is maintained for several minutes.

Extracting the fusion, etc.—When cold, the contents of the dish are extracted in hot water in the manner described for the estimation of chromium on p. 140. The insoluble residue is allowed to settle, and is then collected on a 90 mm. filter-paper, being cautiously but well washed with hot water; the paper is then dried and ignited in a platinum crucible.

Fusing the residue with $HKSO_4$.—The ignited residue is intimately mixed with a few grammes of pure acid potassium sulphate; the crucible is supported on a pipe-stem triangle, and its contents are gently fused over the Bunsen flame for about 15 minutes.

Extracting the sulphate of titanium.—When cold, the crucible is placed in a beaker containing 10 cc. of strong HCl and 50 cc. of sulphurous acid solution, and the whole is *gently* warmed on the plate till the mass is dissolved out, excepting a little insoluble silica. The crucible and cover are rinsed with as little cold water as possible, and when cold the solution is transferred without loss into a 120 cc. flask, is made up to the mark and thoroughly mixed, 100 cc. of the clear fluid corresponding to 5 grammes of iron, and then filtered off.

Precipitating and estimating the titanium.—The liquid is transferred from the graduated flask into a large beaker, and is diluted with hot water to about 1000 cc. The contents of the covered beaker are then slowly boiled down to a volume of 250 cc., when the precipitated metatitanic acid is allowed to settle thoroughly, is filtered off on a close filter, washed with water containing a little sulphurous acid, being dried, ignited, and weighed in the usual manner as TiO_2 containing 60 % of metal. The ignited residue is usually coloured with oxide of iron; this + error is, however, opposed by a — error due to the fact that the precipitation of the titanium is not absolutely completed during the boiling.

Theoretical Considerations.

Titanic acid on evaporation to dryness in the presence of excess of phosphate of iron in nitric acid solution forms an insoluble phosphotitanate of iron. In the absence of sufficient phosphoric acid to fix the titanium in this form, a portion of the TiO_2 passes into the hydrochloric acid solution, thus much complicating the analysis. On fusing the ignited residue, consisting of silica and phosphotitanate of iron, with potassium carbonate, soluble silicate and phosphate of potassium are formed, together with insoluble oxide of iron and trititanate of potassium $K_2Ti_3O_7$. On fusing the mixture of oxide of iron and alkaline titanate with $HKSO_4$, soluble sulphates of iron, potassium, and titanium are formed; on extracting, the SO_2 reduces the ferric to ferrous sulphate. The dilution and prolonged boiling decompose the sulphate of titanium, throwing down a metatitanic acid of uncertain composition, which, how-

ever, yields on ignition TiO_2. In thus precipitating titanium, it is very necessary to have the iron in the ferrous condition, and also phosphoric acid and aluminium salts should be absent from the solution, otherwise the TiO_2 will be seriously contaminated with Fe_2O_3, P_2O_5, and Al_2O_3.

Estimation of Phosphorus in Titanic Irons.

Analysis of the insoluble residue.—To accurately determine the phosphorus in titanic irons, it is absolutely essential to extract the phosphoric acid involved in the insoluble residue, and add it to that obtained in solution in the ordinary manner. This operation is carried out as follows: the ignited residue of silica and phosphotitanate of iron from which the graphite has been burnt off, is fused in the manner described in the last article with an excess of K_2CO_3, the fusion being extracted with hot water and filtered; the filtrate from the insoluble titanate of potash and oxide of iron will contain the phosphorus in solution as potassium phosphate. The clear liquid is made slightly acid with HCl, and a few cc. (say two to ten, according to the richness of the iron in phosphorus) of the standard solution of ferric chloride referred to on p. 117 are added. The acid liquid is heated, made alkaline with ammonia, and boiled. The precipitated phosphate of iron is filtered off, washed with hot water, dissolved in HCl, and the solution is evaporated to dryness. The dry residue is taken up in hydrochloric acid, and the insoluble silica is filtered off; the filtrate containing the phosphoric acid is added to the main solution, in which the phosphorus is then determined as usual.

Analysis of Spiegeleisen and Ferro-Manganese.

These always consist essentially of iron, manganese, and carbon, but also contain on an average 0·75 % *Si*, 0·02 % *S*, 0·25 % *P*, and often a little copper. These four elements are estimated by the respective methods described for steel on pp. 66, 106, 123, 175. The term Spiegeleisen (German, looking-glass iron) is usually contracted to spiegel, and denotes an alloy having a fracture consisting of large bright plates, and containing up to about 30 % of manganese. When the percentage of this metal rises much above this quantity the alloy assumes a granular fracture, and is then known as ferro-manganese. In these alloys, as a rule, the carbon rises with the percentage of manganese, so that in spiegel containing about 15 % mm. the carbon is usually about 4·25 %. In ferro-manganese containing about 50 % *Mn*, the carbon averages 5·5 %, and in an alloy containing 80 % *Mn* the carbon approximates 6·75 %. In spiegel the carbon exists as a double carbide of iron and manganese, in rich ferro-manganese as carbide of manganese.

Determination of Carbon.

The carbon should be estimated by combustion, either by the method described for steel on p. 29 *et seq.*, or by the direct method described on p. 213 for ferro-chrome.

Rapid Indirect Estimation of Manganese.

In large, well-organized Bessemer and open-hearth steel works, where large quantities of spiegel and ferro-

manganese are used, it is usual to approximately check the manganese in the alloys before unloading from the trucks and stacking in the metal yard. Hence, a delivery of 100 tons may have to be passed in a day, necessitating two or three dozen crude determinations.

Sampling.—Break out of each truck six bright pieces of alloy, each about as big as a walnut. These pieces are arranged in pairs, and representative portions from each pair are crushed up together in a steel mortar, passed through a sieve of ninety meshes to the inch, and the powder thus obtained is placed in a dry, numbered sample tube. Thus on the contents of each truck three determinations are made, and an average assay of the six samples is obtained.

The Process.

(Time occupied, about $\frac{3}{4}$ hour.)

Weight taken.—Weigh out into a clean, dry 10-oz. flask exactly 0·5 gramme of the sample.

Dissolving.—Add 100 cc. of pure dilute sulphuric acid, one in seven, cover the flask with a watch-glass, bring the liquid to boiling, and keep it so for twenty minutes, or till the alloy has completely dissolved, and no further evolution of hydrogen is observed.

Titrating the iron.—Rinse the watch-glass, and determine the percentage of iron present by titrating the solution of $FeSO_4$ in the manner described on p. 86 with the standard bichromate specified on p. 184. Each cc. required = 1 % *Fe.*

Calculating the manganese by difference.—To the percentage of iron obtained add the average percentage of elements other than iron and manganese (as indicated in

the following table), deduct the sum from 100, and the difference is the approximate percentage of manganese.

% *Fe.*	Sum of the % of impurities.	% *Mn.*
12·5	7·5	80·0
28·0	7·0	65·0
43·5	6·5	50·0
59·0	6·0	35·0
79·5	5·5	15·0
85·0	5·0	10·0

Example.—The sulphuric acid solution of 0·5 gramme of ferro-manganese required 46·8 cc. of the standard bichromate to completely oxidize the iron to ferric sulphate: then 46·8 + 6·5 = 53·3, and 100 — 53·3 = 46·7 % *Mn.* It will be obvious, that the results thus obtained are always liable to two sources of error, namely, the percentage of impurities may vary somewhat, giving a + or — error, and some solid carbonaceous flocks, and unevolved greasy hydrocarbons, which always remain in the flask, have a slight reducing action on the bichromate, thus producing a — error. However, the author's experience of the process has been, that the percentages of manganese registered are seldom more than 1 % from the truth, an error of no great practical importance to the steel-maker.

Volumetric Estimation of Manganese in Spiegel and Ferro-manganese (Pattinson).

Re-agents required.

Standard solution of $K_2Cr_2O_7$.—This is made up in the manner described on p. 84 by dissolving 8·9225 grammes

of the salt in 1000 cc. of water. The solution is standardized in the manner described on p. 86 by titrating a dilute sulphuric acid solution of 0·51 gramme of Swedish bar-iron, which should require exactly 50 cc. of the bichromate to peroxidize it.

$CaCO_3$ diffused in water.—Place in a Winchester quart 250 grammes of pure precipitated chalk; add two litres of distilled water, and well shake the bottle before pouring off into a beaker a portion of the white fluid as required for use.

The Process for Spiegeleisen.

Weight taken.—Weigh out into a 20-oz. covered beaker 0·5 gramme of the finely-divided alloy. Also weigh out into a dry 12-oz. *very wide-necked* flask 0·51 gramme of standard Swedish iron.

Dissolving.—Pour down the lip of the beaker 25 cc. of strong *HCl*, and gently boil on the plate till the metal has all passed into solution, then add 1 cc. of strong nitric acid, boil, and finally evaporate quietly to very low bulk (not more than 5 cc.).

Neutralizing.—Remove the beaker from the plate, carefully rinse the cover and sides of the vessel, replace the former, and little by little pour down the lip of the beaker the water containing chalk in suspension, constantly shaking round the solution till the free acid is neutralized and a faint red permanent precipitate remains.

Oxidizing and precipitating hydrated MnO_2.—Next add 50 cc. of a saturated aqueous solution of bromine, and then 300 cc. of nearly boiling distilled water; then little by little, with constant stirring, add a few cc. of the chalk

and water, till on the neutralization of the hydrobromic acid a bulky brown precipitate is obtained.

Filtering and washing the precipitate.—Collect the hydrate on a 3-in. ribbed funnel containing a thick German paper, cut so as to project very slightly over the edge. Every particle of precipitate is washed from the rod and beaker, and the filter and its contents are *most thoroughly washed with a jet of nearly boiling water till quite free from hypobromites, etc.*

Titrating.—At the commencement of the washing, add to the flask containing the iron a mixture of 10 cc. of strong H_2SO_4 and 60 cc. of water, and boil the covered flask on the plate till the last particle of iron has dissolved. Remove from the plate, rinse the cover, and very cautiously slide bodily into the acid solution of $FeSO_4$ the paper containing the manganic precipitate. Shake round the contents of the flask till the paper is in pulp, and the dark precipitate has entirely dissolved. The amount of unoxidized iron is then determined in the usual manner by the standard solution of bichromate and the ferricyanide indicator. The number of cc. required subtracted from 50 gives the percentage of manganese present.

Example.—A sample of German spiegel required 35·2 cc. of the standard solution: therefore, $50 - 35{\cdot}2 = 14{\cdot}8\,\%$ manganese.

Theoretical Considerations.

The general principles involved in this process are almost identical with those fully dealt with in describing the Ford and Williams method for the volumetric estimation of manganese in steel on p. 87.

The last-named process may indeed be used for spiegel,

but not for ferro-manganese. But when dealing with such highly manganiferous alloys, Pattinson's process is to be preferred. The oxidation of the manganous oxide to the hydrate of the peroxide is brought about in the neutral solution by the bromine water, but the metal is only entirely thrown down in the form of hydrated dioxide in a hot, dilute solution, containing a considerable excess of ferric iron; the latter condition is of course always present in the case of spiegel. If the precipitate is not freed by thorough washing from bromine and calcium hypobromite, these substances will oxidize the iron, be registered as MnO_2, and so give a high result.

The Process for Ferro-manganese.

Two slight but essential alterations must be made in the foregoing process when dealing with very rich manganese alloys. First, in order to ensure the presence of sufficient iron, only 0·25 gramme of the alloy is weighed out for the analysis, and the finely-divided metal is dissolved up with the addition of half a gramme (weighed roughly) of Swedish iron. To allow for the manganese present in the latter, 0·2 % (= 0·1 % in each 0·25 gramme) must be deducted from the percentage registered. Second, as only 0·25 gramme of alloy is employed for the assay, the result obtained must be multiplied by two.

Example.—On titration, a sample of rich ferro-manganese required 9·8 of bichromate solution, then 50 — 9·8 = 40·2 and (40·2 × 2) — 0·2 = 80·2 % *Mn*.

Gravimetric Determination of Manganese in Spiegel and Ferro-manganese.

(Time occupied, about 1 day.)

Weight taken.—Weigh out into a 20-oz. breaker 0·5 gramme of spiegel or 0·2 gramme of ferro-manganese. To the latter it is convenient to add about $\frac{2}{10}$ gramme of Swedish iron.

Dissolving.—The metal is dissolved by boiling with 25 cc. of strong *HCl*, then add 1 cc. of strong nitric acid, boil well, and dilute to 200 cc. with nearly boiling water.

Neutralizing and precipitating the iron.—The solution is neutralized with dilute ammonia, and the iron precipitated with 20 cc. ammonium acetate in the manner described on p. 72, but in the present case fractional filtration is not employed.

Re-dissolving and re-precipitating the iron.—The basic ferric acetate is collected on a German paper (previously well washed with hot dilute *HCl* and water) contained in a 3-in. ribbed funnel. The beaker is well washed out, and the precipitate is allowed to drain, the filtrate being received in a clean 40-oz. beaker. The funnel containing the iron is next supported on a hanger inside the beaker in which the precipitation took place, and is re-dissolved in the smallest possible quantity of hot *HCl*, the paper being washed in cold water till free from any yellow tinge. The acid solution of ferric chloride is boiled down to about 15 cc., when the liquid is diluted, neutralized, and the iron is precipitated exactly as before. The filtrate is added to that containing the bulk of the manganese (which should in the meantime have been quietly boiled down). The beaker is well rinsed out, and the precipitate is slightly washed with hot water.

Precipitating the manganese.—The two filtrates are boiled down to about 200 cc. to separate traces of iron, and the liquid is filtered into a 30-oz. registered flask; the manganese is then precipitated from the cold solution with bromine and ammonia exactly as described on p. 74.

Igniting, weighing, etc.—When the solution is crystal clear, every particle of the bulky precipitate of manganese dioxide is collected on a 125 mm. pure paper, and is well washed with hot water, and after thoroughly draining is dried, ignited, and weighed in the usual manner. The precipitate, however, must be carefully ignited, otherwise the resulting residue when dealing with such comparatively large weights of oxide will not contain 72 % of manganese Mr. U. S. Pickering has shown that it may contain as little as 70 or as much as 74 % of metal.[1] After the paper has burnt off, the crucible should be kept in the hottest part of the muffle for about half-an-hour; it is then allowed to become quite cold in the dessicator before re-weighing. The weight of precipitate obtained in the case of spiegel when working on 0·5 gramme of the sample is multiplied by 144, and in the case of ferro-manganese when working on 0·2 gramme of metal by 360; the result obtained is the manganese %.

Theoretical Considerations.

The principles of the foregoing method are identical with those described on p. 78 *et seq.* for steel analysis. In the present case, however, it is necessary to re-precipitate the iron to ensure the separation of a small amount of manganese (about 1 %), almost invariably carried down

[1] *Chemical News*, 1881, No. 1121.

on the first precipitation. It will be obvious that when working upon such comparatively small original weights it is necessary to exercise the greatest care during analysis to avoid the introduction of any manipulative errors, because the latter would be respectively multiplied by two and five instead of being diminished by distribution over a large original weight. The addition of a little Swedish iron to the ferro-manganese enables the neutralizing operation to be carried out with greater certainty than when only the small amount existing in the sample *per se* is present. The results obtained by the volumetric and gravimetric methods agree very well when the respective processes have been carefully carried out.

Analysis of Ferro-chrome.

An accurate complete analysis of this material is a matter presenting considerable difficulties. The rich alloy used for the manufacture of special steels contains from 40 to 65 % of chromium, and 7 or 8 % of carbon, and is not completely soluble in acids.

Sampling.—Representative pieces must be reduced to a granular condition by crushing in a steel mortar, and passing through a sieve of 90 meshes to the inch. The comparatively coarse metallic powder thus obtained then requires to be converted into an impalpable flour by treating it a few tenths of a gramme at a time in an agate mortar. The success of the analysis depends in a great measure upon having the alloy in an excessively fine state of division, necessitating a very tedious pulverizing operation to obtain enough of the floured material for a complete analysis, as at least 5 grammes will be required.

Determination of Chromium.

Gravimetric Process.

This is carried out by the hydrate method described on p. 138, by mixing in a 3-in. platinum dish ·12 gramme of the metallic flour with 5 grammes of the fusion mixture, and maintaining the fused mass in a liquid state over a powerful Bunsen for half-an-hour, when the chromium will be completely converted into alkaline chromate. The process when skilfully carried out gives accurate results, but the small original weight necessarily taken to obtain a readily washed precipitate makes a small manipulative error serious. Hence it is, as a rule, best to use the volumetric process next dealt with, which has the additional advantage of being quickly carried out.

Volumetric Method (Clark and Stead).

Re-agents required.

Tribasic dry fusion mixture.—Intimately mix and bottle for use—

50·0 grammes pure calcined magnesia (MgO).
12·5 grammes pure K_2CO_3.
12·5 grammes pure Na_2CO_3.

Standard solution of $K_2Cr_2O_7$.—Dissolve 14·155 grammes of pure bichromate in 1000 cc. of water.

The Process.

(Time occupied, about 3 hours.)

Weight taken.—Weigh out into a 2½-in. diameter flat platinum dish 0·5 gramme of the floured alloy, and by means

of a glass rod *very intimately* mix with 10 grammes of the tribasic re-agent. Carefully brush any adhering powder from the rod into the dish, and then gently tap down the mass.

Dry fusion.—Having heated the dish for a few minutes in the middle of the hot plate to drive off any hygroscopic moisture, introduce it into the muffle, and heat in the hottest part for two hours, when the metal will have become completely oxidized to chromate.

Extracting the fusion.—Introduce the dish when cold into a clean 20-oz. covered beaker, and pour down the lip a mixture of 25 cc. strong sulphuric acid with 150 cc. of water. Heat till all soluble matter has passed into solution, and only a small residue of oxide of iron remains; the dish is then washed and removed. The liquid should be of a clear yellow colour.

Titrating.—When the extraction is commenced weigh out into a 20-oz. dry flask 1·618 grammes of Swedish iron, and dissolve in a mixture of 20 cc. strong sulphuric acid and 120 cc. of water. When the solution is complete, rinse the watch-glass, and transfer to the flask every trace of the yellow liquid in the beaker. The excess of ferrous iron is then determined as on p. 86. The number of cc. used subtracted from 100 gives the percentage of chromium present; in other words, each cc. left corresponds to 1 % of chromium.

Example.—A sample of Hanoverian ferro-chrome required on titrating back 35·7 cc. of bichromate, then 100 — 35·7 = 64·3 % *Cr.*

Theoretical Considerations.

The theoretical principles involved in this process are almost identical with those described on p. 155 in connection with the volumetric estimation of chromium in steel. On extracting the dry fusion from which nitrates were absent, the chromic acid CrO_3 remains unreduced by the dilute sulphuric acid employed, whereas, had nitrites been present as in the wet process, the anhydride would have been at once reduced to chromic oxide Cr_2O_3, which change in the present case is brought about by the ferrous iron, the oxygen yielded and consequently the chromium present being measured by difference on estimating the excess of FeO by the standard solution of $K_2Cr_2O_7$.

Determination of Silicon.

(Time occupied, about 4 hours.)

The determination of silicon is carried out working upon 2 grammes of the floured alloy in the manner described for chrome steels on p. 68.

Estimation of Sulphur.

This may be determined with sufficient accuracy for practical purposes by treating 3·6 grammes of the alloy which has passed through the 90-mesh sieve with 100 cc. of aqua regia. The solution is boiled down to low bulk in a 20-oz. covered beaker, the evaporation is then gently continued to complete dryness. The dry mass when cool is taken up in HCl, evaporated to low bulk, transferred to

a 60 cc. flask, and 50 cc., corresponding to 3 grammes of alloy, are filtered off in the usual manner, and the sulphur is estimated by the gravimetric process described for steel on p. 96. The insoluble residue remaining with the $\frac{1}{6}$ of unfiltered solution is, as a rule, practically] free from sulphur.

Estimation of Phosphorus.

3·6 grammes of the alloy, after being passed through the 90-mesh sieve, are treated as in the case of the sulphur determination. The 50 cc. of liquid containing the phosphorus in 3 grammes of the alloy, are evaporated to low bulk, made alkaline with ammonia, acid with 1·42 nitric acid, and the phosphorus is approximately determined as ammonio-phospho-molybdate in the manner described on p. 124.

Determination of Manganese.

(Time occupied, about 1 day.)

Weight taken.—Weigh out 1·2 grammes of the floured alloy into a 3-in. platinum basin, containing 20 grammes of the wet fusion mixture described on p. 138.

Fusing.—Very intimately incorporate the mixture, and fuse for an hour over a powerful Bunsen burner.

Extracting.—When cold, extract the mass as described on p. 140, the chromium will then be in solution as chromate, and the iron and manganese will be precipitated respectively as peroxide and hydrate.

Removing most of the chromium.—Allow the precipitates to settle somewhat, and then pour off as much as possible of the yellow liquid through a 110 mm. pure paper.

Neither the filter nor beaker need be washed, but the lip of the latter should be rinsed.

Dissolving up the manganese and iron.—Place the funnel in a hanger inside the beaker in which the extraction took place, and treat it with strong warm HCl. Any hydrate of manganese will readily dissolve, and the filter is then washed with water, ignoring any finely-divided and not readily soluble Fe_2O_3 in its pores. Remove the funnel and boil the liquid in the covered beaker to low bulk, when the manganese together with most of the iron and a very small portion of the chromium originally present will be in solution as chlorides.

Remaining operations.—The solution is diluted with hot water, neutralized with ammonia, and the iron is precipitated on boiling with ammonium acetate. The liquid and precipitate are transferred to a 300 cc. flask, 250 cc. are filtered off, and from this liquid the manganese in 1 gramme of the alloy is precipitated with bromine and ammonia. The details of the above operations have already been described on p. 72 *et seq.*

Theoretical Considerations.

The principles involved in the foregoing analysis will be clear to the student after studying the theoretical notes attached to the articles describing the estimation of manganese and chromium in steel respectively on pp. 78 and 143. The large amount of chromium and the comparatively small quantity of iron present in ferro-chrome render necessary the preliminary separation of most of the first-named metal from the iron and manganese, otherwise some Cr_2O_3 is thrown down with the final precipitate.

Determination of Carbon by Direct Combustion.

Carbide of chromium is not attacked by $CuCl_2$, hence it is necessary to directly burn off the carbon from the alloy. For this purpose two conditions are absolutely essential—

1. The metal must be in the finest possible state of division attainable in the agate mortar.

2. The temperature of the combustion in *moist oxygen* must be at a full red-heat, consequently selected tubing of the most refractory glass obtainable must be employed for the combustion. The average combustion tubing sufficiently refractory to perfectly burn off liberated carbon is quite useless in the present case.

The Process.

(Time occupied, about 3 hours.)

Weight taken.—Very carefully weigh out exactly 0·5 gramme of the metallic flour.

Mixing with $PbCrO_4$.—Place 10 grammes of finely-powdered, recently fused [1] chromate of lead in a 3-in. porcelain dish. Into a hollow in the heap of chromate very carefully introduce, by gently tapping and brushing the foil, every particle of the half gramme of ferro-chrome. The two substances are then very intimately mixed by means of a glass rod. This operation should be conducted after placing the dish on a sheet of glazed white paper, so that any accidentally projected powder may be safely recovered.

[1] This fusion should be gently conducted in the muffle, the chromate being contained in a porcelain dish.

Packing the combustion tube.—Into the perfectly clean, very hard glass combustion tube, which should be about 700 mm. long and 20 mm. inside diameter, *firmly* place a plug of recently-ignited asbestos, 20 mm. long, 250 mm. from one end, into the longer portion of the tube thus divided; very carefully, by means of a small spatula and sable-hair brush, introduce the mixture from the dish, rinsing the latter out twice with 2 or 3 grammes of fresh, ignited oxide, and shake the whole well down into the combustion tube. Push up to within 2 mm. of the powder another 20 mm. asbestos plug which carries down any substance adhering to the sides of the tube. The small space left between the powder and the last plug serves, when the tube is in a horizontal position, to leave a channel at the top of the mixture for the passage of the gases. The upper side of the plug, next the middle of the tube, is now gently perforated with a pointed wire for the same purpose, the tube being placed during this operation in a horizontal position. It is next held vertically with the unperforated plug downwards, and another tightly-packed plug of asbestos is inserted to within 5 mm. of the perforated plug. Having gently made a passage through the asbestos last inserted, pour in sufficient ignited oxide of copper scales to form a column 150 mm. long. Secure the compactness of the column with a final plug of asbestos: perforate it, and that first inserted, and all is ready for the combustion (see Fig. 16).

Fig. 16.

The Combustion.—This is carried out exactly as described

for the cupric chloride residue, except that the heating is prolonged, and is made as intense as possible. It is also advisable to have in the end of the combustion tube, next the gas-holder, some loose fragments of slightly moistened asbestos, so that the oxygen may be saturated with aqueous vapour, which will materially assist the combustion.

Theory of the Process.

The elements present in the alloy in contact with the chromate of lead at a full red heat are all converted into oxides, the carbon thus—$C + 2\,PbCrO_4 = 2\,Pb + Cr_2O_3 + CO_2$. The metallic lead in the presence of oxygen is at once converted into oxide, thus— $Pb + O = PbO$. With reference to the use of moist oxygen, the author recommends this, because in 1880, whilst attempting to estimate as water the hydrogen in steel by combustion in chemically dry oxygen, he found that the fine steel drillings remained bright and unoxidized, although exposed to a full red heat in the gas. In moist oxygen the steel burnt readily enough. By introducing a known weight of moisture, several results were obtained which indicated the presence of an appreciable percentage of hydrogen, but they were not concordant.

Analysis of Ferro-silicon.

This alloy usually ranges in silicon from 10 to 20 %.

Determination of Silicon.

The estimation is made on 1 gramme of the crushed alloy, passed through a sieve of 90 meshes to the inch.

The method is identical with that described for pig-iron on p. 189. The ignited SiO_2 is, however, seldom quite white, and it is therefore best to ignite it in an untared platinum dish, and then intimately mix and well fuse the impure residue in the covered dish with a few grammes of pure acid potassium sulphate. The purified silica is then determined in the manner described on p. 68.

Estimation of Carbon.

The carbon in ferro-silicon exists chiefly as graphite, and the total may range from 0·2 to 2 %. As the alloy is absolutely unattacked by cupric chloride, the carbon must be determined by the direct combustion of 1 gramme of the finely-floured alloy in the manner described for ferro-chrome on p. 213.

Estimation of Manganese, Sulphur, and Phosphorus.

These elements are determined by the methods already given for the analysis of pig-iron.

Analysis of Ferro-aluminium.

The alloy used in steel and iron foundries seldom contains more than 10 % of aluminium. It is often very impure, and its general analysis is carried out as in the case of pig-iron.

Estimation of Aluminium.

(Time occupied, about 1 day.)

Weight taken.—Weigh out into a 20-oz. beaker 0·6 gramme of the finely-divided alloy, passed through a sieve of 90 meshes to the inch.

Dissolving.—Dissolve the metal in 30 cc. of strong HCl; evaporate to dryness, and take up in HCl.

Filtering off the insoluble residue.—The residue is collected on a 90 mm. paper, the filter being well washed with HCl and water. The filtrate and washings are received into a clean 30-oz. registered flask.

Precipitation as phosphate.—The acid solution is diluted to 150 cc., is neutralized with dilute ammonia, reduced with sulphurous acid (25 cc.), and the sulphurous acid is boiled off. Then add 12 cc. of the standard solution of sodium phosphate mentioned on p. 167. This quantity will be sufficient to precipitate as phosphate 15 % of aluminium on 0·5 gramme. Next add to the boiling liquid 5 cc. of acetic acid, and gradually 25 cc. of hot ammonium acetate solution. Boil for a few minutes, remove the flask from the plate, and allow the precipitate to settle.

Filtering off and re-dissolving the phosphate.—The precipitate is collected on a 125 mm. pure paper contained in a 3-in. funnel: the flask is rinsed out, and the paper and its contents are slightly washed. The funnel is then supported on a hanger inside a 20-oz. beaker, and the filter is treated with strong hot HCl, heated in the flask in which the precipitation took place, till the phosphates have dissolved, when the filter is well washed. The smallest possible quantity of acid and wash-water should, however, be used.

Separating the iron.—The yellowish solution is boiled down to low bulk, and finally, *very gently* evaporated almost to dryness. The co-precipitated iron is then separated from the aluminium by pure sodic hydrate in the manner described on p. 170. The fraction of five-sixths of clear liquid contains the aluminium in 0·5 gramme of the alloy.

Remaining operations.—The liquid is transferred to a 20-oz. beaker, acidified with *HCl*, and the phosphate of alumina is thrown down with a faint excess of ammonia, digested, filtered off, and washed. It is, however, advisable in the present instance to re-dissolve the precipitate in hot *HCl*, well wash the filter, collecting the solution and washing in a 20-oz. beaker; the acid liquid is then brought to boiling after the addition of about a gramme of ammonium phosphate, and dilute ammonia is added little by little down the lip of the covered beaker till the acid is neutralized, and a faint excess of alkali present. After digesting till the liquid is clear, the flocculent phosphate is collected, washed, dried, ignited, weighed, and its percentage calculated on ·5 gramme of the alloy, in the manner described on p. 171 for the estimation of aluminium in steel.

Theoretical Considerations.

The theory of the foregoing process has been fully dealt with in connection with steel. The details which differ are, first, that in the present case the comparatively small quantity of iron present renders unnecessary a second precipitation with ammonium acetate; second, the comparatively large weight of the aluminium precipitate

renders the thorough removal from it of the fixed alkalies by washing difficult, hence the second precipitation with ammonia.

Analysis of Aluminium Metal.

This product is now obtained so pure that the presence of more than 1 % of foreign elements is unusual. The latter consist mainly of iron and silicon.

Estimation of Silicon.

Silicon is determined on 2·4 grammes of drillings exactly as in the case of steel, but before filtering the solution containing the chlorides of aluminium and iron, it is evaporated to low bulk with the previous addition of two drops of strong HNO_3. The concentrated liquid when cold is washed into a 60 cc. flask, diluted to the mark, thoroughly mixed, and 50 cc. of the fluid are filtered into a graduated flask. The solution thus obtained, containing the iron in 2 grammes of aluminium, is set aside to be used for the determination of the iron in the manner described in the next article. The filtration of the SiO_2 is then continued in the usual manner. It is washed, dried, ignited, and weighed, and the percentage of silicon is calculated on 2·4 grammes.

Determination of the Iron.

On a convenient known volume measured from the 50 cc. of acid solution containing the iron in 2 grammes of aluminium obtained as described in the last article, the percentage of iron present is determined colorime-

trically by means of the alkaline sulphocyanide by the process described on p. 75.

ANALYSIS OF FERRO-TUNGSTEN.

This alloy usually contains about 33 % of tungsten.

Determination of Tungsten and Silicon.

These elements are determined on 1 gramme of the finely-divided sample by the process given for self-hardening steels on p. 133.

Estimation of Carbon.

The carbon is determined on 1 gramme of the finely-floured alloy by the direct combustion process described on p. 213 for ferro-chrome.

Estimation of Manganese, Sulphur, and Phosphorus.

These elements are determined by the processes given for tungsten steels respectively on pp. 83, 96, 128.

ANALYSIS OF METALLIC TUNGSTEN.

The metal in the form of a heavy grey powder is now obtainable, registering up to 98 % of tungsten.[1] The assay for the total metal is made on ·6 gramme of the

[1] Small quantities of niobium are sometimes present.

floured substance weighed out into a platinum dish, and cautiously ignited in the muffle or over a powerful Bunsen flame (to convert the metal into oxide) by the process described on p. 270 for wolfram.

Examination of the metal for Oxides.

Although the total yield of tungsten in commercial metals may seem fairly satisfactory, it does not follow that the whole of it represents actual reduced metal. The high atomic weight of tungsten renders possible the presence of the considerable percentage of oxides without apparently seriously impairing the value of the product as determined by assay. The author some years ago found an alleged sample of metallic tungsten to contain over 25 % of oxides. The material when reduced in dry hydrogen gave off water in well-defined fractions, corresponding to the sequence of the reduction of the oxides. First, at a low red heat, the powder assumed a deep, brilliant blue colour, due to the reduction of the WO_3 present to the blue oxide ($2\ WO_3 + WO_2$), and drops of water speedily collected in the cooler portion of the combustion tube. Second, as the temperature rose, the blue changed to a rich purplish-brown, corresponding to the production of the oxide WO_2, more water being given off. It was found impossible to complete the reduction of the brown oxide to metal at the highest temperature of the Hoffman furnace. For this purpose the material must be heated to a white heat in a porcelain tube in a current of hydrogen. A crude but useful qualitative test for oxides is to gently boil 10 grammes of the metallic powder with 10 cc. of strong HCl; the metal is allowed to settle, and the nearly clear

supernatant liquid is decanted off into a 50 cc. measure. On filling up the latter with distilled water, if any considerable quantity of oxides are present, a blue colour will be developed, and after a little time, a deep blue, greenish, or yellowish precipitate of the oxides of tungsten will precipitate from the solution.

Analysis of Ferro-Nickel.

The general analysis of this material is carried out as though dealing with a pig-iron. In the determination of manganese the precautions described on p. 83 must be observed. The presence of nickel does not interfere with the volumetric estimation of manganese described on p. 84.

Determination of Nickel.

The percentage of nickel in ferro-nickel may, with care, be estimated sufficiently accurately for practical purposes on 0·24 gramme of drillings or crushed metal by the process described for steel on p. 160, the result being of course calculated on 0·2 gramme. The assay may also be made by the electrolytic process described in the next article.

Analysis of Metallic Nickel.

This product when in cubes may contain some unreduced oxide, and more or less carbon, silicon, copper, manganese, sulphur, iron, and cobalt are usually present. The metal last named may be safely ignored in steel

works' practice, any small amount present being co-precipitated with the nickel and recorded as such. Ingot nickel may be drilled for analysis, but if in the form of cubes or large shots, if possible one or two lbs. of the latter should be fused in a clay crucible and cast into a small ingot for drilling; otherwise the metal is very awkward to sample for analysis, the only way being to dissolve up one or two weighed cubes or a few shots in *aqua regia*: several grammes may be thus totally dissolved, but only after prolonged digestion. The liquid is evaporated to dryness, the mass taken up in HCl, and the solution when cold is made up to exactly 250 cc., the liquid being thoroughly mixed. From this a volume of filtered solution corresponding by calculation to the desired weight of actual metal is carefully measured out for analysis from a delicately graduated burette.

Electrolytic Estimation of Nickel.

(Time occupied, about $1\frac{1}{2}$ days.)

Weight taken.—Two grammes of metal are weighed or measured into a 20-oz. covered beaker.

Dissolving.—The drillings are dissolved by boiling with 30 cc. of *aqua regia.* The solution is evaporated to dryness, and re-dissolved in 50 cc. of dilute sulphuric acid one in six. The solution is again concentrated till white fumes of sulphuric acid are evolved; the contents of the beaker are cooled, and 40 cc. of cold water are next cautiously added down the lip of the covered beaker, and the contents of the vessel are boiled till every trace of the precipitated sulphate of nickel has passed into solution. The liquid is then diluted to 150 cc. with nearly boiling water.

Separating the copper.—The copper is next precipitated as CuS by passing through the hot liquid a brisk current of washed H_2S for about fifteen minutes. The precipitate is filtered off on a 90 mm. pure paper, the latter and its contents being well washed with water containing H_2S and about 1 % sulphuric acid. The filtrate and washings are received into a clean 30-oz. registered flask.

Separating the manganese and iron.—Cool the acid filtrate, add 2 cc. of bromine, and shake round until it has dissolved. Then add 50 cc. of strong ammonia, shake the solution vigorously round, and digest the deep blue liquid till the hydrates of manganese and iron have flocked out. Collect the precipitate on a 90 mm. pure filter, and wash the latter thoroughly with hot water. The filtrate and washings are received into a 300 cc. graduated flask, and when cold, are made up to the mark and thoroughly mixed.

Removing ammonium bromide.—Carefully measure off from a burette 37·5 cc. of the blue solution corresponding to 0·25 gramme of metal into a 4-in. porcelain dish, quietly evaporate on a sand-bath till the salts begin to separate, add 50 cc. of dilute sulphuric acid, and again evaporate till white fumes are evolved. The precipitated sulphate of nickel is re-dissolved in the smallest possible quantity of water, is transferred without loss to a 3-in. deep platinum basin previously cleaned both inside and out, heated in the air-bath, and cooled and weighed.

Depositing the nickel.—The liquid is then made strongly alkaline with ammonia, when the total bulk should be about 30 cc., and the nickel is electro-deposited by connecting it over-night with the arrangement sketched in Fig. 17. The wooden stand A carries a brass rod B with brass screws at each end; the platinum basin is

placed on a bright platinum plate on the base of the stand connected with the binding screw C. One end of the brass rod carries a stout platinum wire attached to a perforated platinum plate, the latter being immersed in the alkaline solution of nickel sulphate. A battery of three or four pint Daniell cells, well charged in the

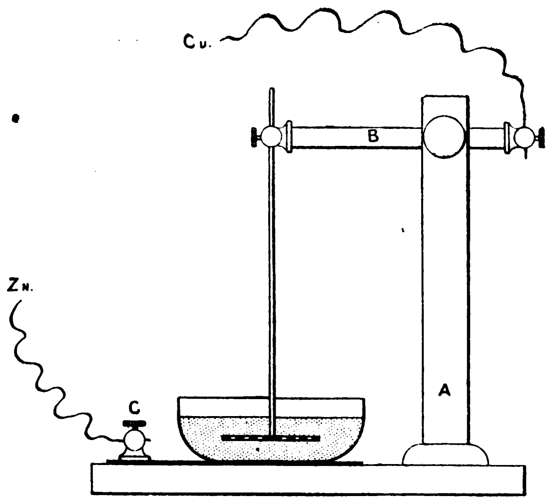


FIG. 17.

shelves with crystals of cupric sulphate, will be required.[1] The copper terminal of the battery is attached to the brass rod, whilst the zinc pole is coupled up with the screw C by means of stout insulated copper wire. In a few hours the whole of the nickel should be deposited

[1] Where possible, electrolysis should be effected from storage cells, the most favourable strength of current previously determined by experiments being maintained by the interposition of a suitable galvanometer in the circuit.

as a closely adherent bright reguline lining in the tared dish. The complete deposition of the nickel is proved by bringing a very small drop of the ammoniacal liquid (taken up in the capillary tube at the end of a drawn-out $\frac{1}{8}$-in. glass tube) into contact with a small drop of a saturated solution of H_2S water placed on a white slab. As long as any nickel remains in solution a brown colour is produced.

Weighing the nickel.—When the deposition is complete, the dish is withdrawn and thoroughly washed with nearly boiling distilled water. It is dried in the air-bath at 100° C., cooled in the desiccator, and re-weighed. The increase over the first weighing multiplied by four gives the percentage of nickel.

Rapid Method.

The foregoing method is tedious, and the result obtained is usually slightly low, owing to the precipitates of copper and manganese carrying down with them traces of nickel. In the majority of cases, sufficiently accurate results may be obtained by dissolving 2 grammes of the nickel in dilute sulphuric acid, evaporating the solution till copious white fumes appear, and then, with the usual precautions, obtaining the sulphate in a volume of 300 cc.; 37·5 cc. of the filtered liquid are then electrolyzed as before described. The metal obtained may be slightly contaminated with copper and iron, but the manganese will be precipitated in the solution as hydrated peroxide.

Estimation of Impurities.

The impurities in commercial metallic nickel are determined by the methods already described in connection with steel. The iron, however, may be estimated colorimetrically with an alkaline sulphocyanide, being previously precipitated as hydrate by means of ammonia, and then obtained in dilute HCl solution. The details of this process will be sufficiently obvious after reading the method described on p. 76, the result being calculated to metallic iron.

Carbon is estimated by combustion by the cupric chloride process. Heat will be required for dissolving the nickel, and no copper will be precipitated owing to the formation of a soluble double sub-chloride.

Silicon is determined on the residue obtained after the evaporation to dryness in *aqua regia.*

Copper is estimated after precipitation with H_2S from a dilute HCl or H_2SO_4 solution by the process described on p. 175.

Manganese is best determined gravimetrically (with the precautions given on p. 83) on the precipitate obtained with bromine and ammonia in the manner described in the last article but one, the iron being of course separated as usual with ammonium acetate.

Sulphur is estimated by the *aqua regia* process.

SECTION II. ORES.

ANALYSIS OF IRON ORES.

THE industrial ores of iron may be roughly divided into three classes—

1. Ferric oxides. Type, hematite $Fe_2O_3 = Fe$ 70 %, O 30 %.

2. Ferroso-ferric oxides. Type, magnetite Fe_3O_4 or $(FeO, Fe_2O_3) = Fe_2O_3$ 69 %, FeO 31 %, Fe 72·4 %.

3. Ferrous carbonates. Type, clay ironstone $FeCO_3$ or $(FeO, CO_2) = FeO$ 62 %, CO_2 38 %, Fe 48·2 %.

(Calcined clay iron-stone may be regarded as an artificial hematite.)

These ores, it need hardly be stated, are, so far as commercial quantities are concerned, never to formula. They always contain more or less of the following impurities—silica SiO_2, alumina Al_2O_3, manganous oxide MnO, peroxide of manganese MnO_2, phosphoric acid P_2O_5, sulphuric acid SO_3, iron pyrites or ferric sulphide FeS_2, lime CaO, magnesia MgO, moisture and combined water H_2O, and organic matter; often, also, titanic acid TiO_2 is present. There may sometimes exist in the ore either the oxides or sulphides of the following metals: chromium, arsenic, copper, nickel, lead, zinc, barium, vanadium, potassium, and sodium.

The foregoing, in addition to CO_2, FeO, and Fe_2O_3, constitute a formidable-looking list, and if it were necessary in practical work to follow the elaborate scheme of analysis sometimes formulated, of estimating every trace of every element, and assigning to it its actual form of existence in the ore, the world would have to wait for its iron. In the great majority of cases it is only requisite to determine as nearly as possible the following substances:

Iron, existing as Fe_2O_3.

Iron, existing as FeO.

Manganese, best calculated to MnO_2 in oxides, and to MnO in carbonates.

Silicious residue, sometimes reported as SiO_2, but often impure, containing small quantities of oxide of iron, alumina, titanic acid, lime, magnesia, and rarely potash and soda.

Phosphorus, existing as P_2O_5.

Arsenic.

Sulphur, existing partly as SO_3 (in which form it is usually reported), but sometimes chiefly as FeS_2.

Alumina, Al_2O_3.

Lime, CaO.

Magnesia, MgO.

Carbonic acid, CO_2.

Hygroscopic moisture.

Combined water and organic carbon.

After describing fully the methods by which the items in the above list are estimated, the author will deal more briefly with the determinations of chromium, copper, and nickel, the analysis of the silicious residue, the approximate estimation of titanic acid, and the alkalies.

Sampling the Ore.

It is far easier to make an accurate analysis of the ore than to ensure the selection of an absolutely representative sample. This must depend in a great measure upon the judgment of the analyst when this duty devolves upon him. It is only possible to advise a judicious selection of representative pieces from different parts of the parcel, and again taking from these smaller pieces, and crushing and mixing the whole of the latter. Of course, aggregated crystals of quartz, calcite, pyrites, apatite, etc. must be avoided, and yet the attempt must be made to obtain a fairly representative percentage of these in the sample. The latter, after being coarsely powdered in a large clean iron mortar, should at once be placed in a well-stoppered, wide-mouthed bottle.

DETERMINATION OF MOISTURE.

(Time occupied, about 1 day.)

This constituent being liable to change in a warm laboratory, should be determined at once. Clean a shallow platinum or porcelain dish about 3 in. in diameter, heat it slightly, and allow to cool in the desiccator. When cold, introduce about 20 grammes of the ore, and ascertain the exact weight of the dish + ore. Place them in an air-bath, and heat for several hours at 100° C., till the weight of two consecutive weighings made at an interval of an hour are practically identical, the dish and its contents before each weighing having been of course allowed to go quite cold in the desiccator: the difference between the original and final weighings is hygroscopic water.

The whole of this dry ore may now be finely pulverized in a Wedgwood ware mortar, passed through a 90 mesh sieve, transferred to a dry, wide-mouthed stoppered bottle, and be employed throughout for the determination of the other constituents, the percentages of which will have reference to the ore dried at 100° C., and not to the original sample, upon which, however, the results may be ultimately calculated if desired.

Estimation of the Total Iron.

For hematites, magnetites, and clay ironstones practically completely decomposed by hydrochloric acid, and containing only a small percentage of organic matter, this is a rapid process occupying only about an hour, and is applicable to the great majority of ores.

The Method.

Weight taken.—Carefully weigh out and transfer to a clean, dry 10-oz. flask 0·5 gramme of the finely-divided ore.

Dissolving.—Add 25 cc. of strong hydrochloric acid, put a watch-glass on the flask, and boil till the insoluble residue is fairly white. In ores high in silica the flask is best heated on a pipe-stem triangle, otherwise the flask is liable to bump or spit.

Oxidizing organic matter.—If the ore contains any appreciable percentage of organic matter, cautiously add to the solution about a gramme of chlorate of potash crystals, and continue the boiling till the smell of the liberated chlorine has disappeared.[1]

[1] This treatment will not suffice for black-band ores, the analysis of which will be dealt with later on.

Neutralizing.—Rinse the cover and inside of the flask with distilled water, and slowly add dilute ammonia solution, constantly shaking round the flask till a faint permanent precipitate is obtained.

Reducing.—Next pour round the inside of the flask 25 cc. of strong sulphurous acid solution and then 50 cc. of water. Boil the diluted solution till *free from every trace of* SO_2. The liquid should have a faint sea-green colour quite *free from any tinge of yellow.*

Titrating.—Add to the ferrous solution 10 cc. of dilute sulphuric acid (1 in 7), remove the flask from the plate, and determine the iron present in the manner set forth on p. 86 by means of the standard solution specified on p. 184. Each cc. of bichromate used = 1 % of metallic iron in the half gramme of ore. If the material under examination is a hematite or magnetite, 50 cc. of the standard solution may as a rule be at once run into the flask, as in such ores the metal does not usually fall below 50 %. If an uncalcined clay ironstone or a spathic carbonate is being analyzed, it is generally safe to run in 30 cc. without over-shooting the mark.

Theory of the Process.

The hydrochloric acid converts the oxides of iron into their respective chlorides, thus—

$$FeO + 2\ HCl = FeCl_2 + H_2O$$
$$Fe_2O_3 + 6\ HCl = 2\ FeCl_3 + 3\ H_2O$$

From carbonated ores the CO_2 is evolved thus—

$$FeCO_3 + 2\ HCl = FeCl_2 + CO_2 + H_2O$$

The addition of the $KClO_3$ to the HCl causes an evolution of a mixture of chlorine and its oxides, which in the

presence of organic matter and water liberate from the latter nascent oxygen, which converts the carbonaceous matter (when only moderate in quantity) into CO_2 and water.

Otherwise readily oxidized organic matter might have a reducing action on the bichromate, and so cause the result to be registered somewhat too high. The reasons for neutralizing the solution before reduction, and for adding a little sulphuric acid before the titration, have already been given respectively on pp. 88, 120, whilst the theory of the titration itself has been fully explained on p. 88. The reducing action of the SO_2 is formulated on p. 120.

DETERMINATION OF FERROUS OXIDE.

The exact amount of FeO present in an ore can only be estimated when peroxide of manganese is absent. The latter compound oxidizes or chlorinizes acid solutions of ferrous salts to the ferric condition, thus—

$$MnO_2 + 4\ HCl + 2\ FeCl_2 = MnCl_2 + 2\ FeCl_3 + 2\ H_2O$$

or

$$MnO_2 + 2\ H_2SO_4 + 2\ FeSO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2\ H_2O$$

Therefore in ores containing MnO_2 the percentage of FeO registered will be more or less low.[1]

On the other hand, in ores containing much carbonaceous matter and no dioxide of manganese, the result obtained may be high, owing to the action of any easily oxidized organic matter in reducing the bichromate solution, when

[1] Conversely it follows, that in the presence of ferrous iron it is not possible to accurately determine the percentage of dioxide of manganese present, when measured by the chlorine evolved on treating the ore with hydrochloric acid, thus—

$$MnO_2 + 4\ HCl = 2\ Cl + MnCl_2 + 2\ H_2O$$

the oxygen thus absorbed would be recorded as due to the oxidation of ferrous salt. It is usual to make an approximate estimation of ferrous iron so as to balance the analysis in the cases of magnetites, raw carbonates, calcined carbonates (in which to some extent the *FeO* is a measure of the thoroughness of the calcination, after which operation the iron should exist almost totally in the ferric condition), and in certain brown hematites (such as those of Northamptonshire), which have resulted from the more or less complete decarbonation and oxidation of original deposits of impure ferrous carbonate. In red ores and in most brown hematites the estimation of *FeO* is not often a matter of any importance.

Apparatus required.

Fit a 10-oz. flask with a clean india-rubber stopper perforated with one hole, in which is inserted a piece of glass tubing 2″ long by $\frac{1}{8}$″ inside diameter. Upon this slip a piece of india-rubber tubing 3″ long, and closed at one end with about $\frac{3}{4}$″ of glass rod. In the space between the glass tube and the rod there must be cut very cleanly, with a keen penknife, a vertical slit about $\frac{1}{2}$″ long. This is best made whilst the india-rubber tubing is distended on a piece of glass rod. The opening acts as a valve allowing gases evolved from the interior of the flask to escape into the air, but preventing the latter from entering the flask, thus avoiding during the dissolution any atmospheric oxidation of the ferrous salt.

The Process.

(Time occupied, about half-an-hour.)

Weight taken.—Place exactly half a gramme of the very finely-divided ore in the clean and dry 10-oz. flask. Next add 2 or 3 tenths of a gramme of pure dry sodium carbonate (Na_2CO_3).[1]

Dissolving.—Add 25 cc. of strong HCl, and quickly insert the india-rubber stopper and valve. Heat the contents of the flask as rapidly as safely possible, and maintain at a gentle boil till the insoluble matter is fairly white, then take off the plate.

Diluting.—Remove the stopper, and add promptly 100 cc. of recently-boiled water, then rinse the stopper and sides of the flask.

Titrating.—Test a drop of the solution with a drop of the very dilute solution of potassic ferricyanide placed on the white slab to see if the blue colour indicative of the presence of FeO is produced; if not, the iron in solution exists totally as ferric chloride. If, however, the ferricyanide shows that ferrous iron is present, proceed to titrate the liquid exactly as in the case of the assay for the total iron. The volume of bichromate used will vary with different ores. Certain very pure spathose ores may require 45 cc., equivalent to 45 % of metal, or about 58 % of FeO. Magnetite will not often require much more than 20 cc., equal to 20 % Fe, or about 25 % FeO, whilst hematites or calcined carbonates may not take more than 1 cc., showing that only about $1\frac{1}{4}$ % of FeO is present.

[1] This on the addition of the acid expels the air in the vicinity of the liquid, thus reducing the chances of atmospheric oxidation of the latter.

Conversion of cc. $K_2Cr_2O_7$ to % FeO.—To convert the cc. of standard solution required, which are each equivalent to 1 % of metallic iron, to their corresponding percentage of *FeO, multiply by* 1·2857.

Calculation of the Ferric Oxide.

The total iron having been determined, and (approximately) the metal existing in the ferrous state, the difference between the two is necessarily (approximately) the iron present as ferric oxide. Therefore from the number of cc. required by the total iron, subtract the volume run in for the ferrous iron; the remainder is the percentage of metal existing in the ferric condition. This multiplied by 1·4286 gives the percentage of Fe_2O_3. The following example will show how the above factors are obtained:—

$$FeO = \begin{cases} Fe = 56 \\ O = 16 \end{cases} \quad \underline{72} \qquad \text{Then } \tfrac{72}{56} = 1{\cdot}2857, \text{ or } 56 \times 1{\cdot}2857 = 72$$

Example showing Titrations of a Swedish Magnetite.

cc. taken by total iron = 55·3 = % *Fe*.
„ „ ferrous „ = 18·9 = „
„ „ ferric „ = 36·4 = „
18·9 × 1·2857 = 24·34 = % *FeO*.
36·4 × 1·4286 = 52·00 = % Fe_2O_3.

Determination of Total Iron in Raw Black-band Ores.

The variety of ferrous carbonate known by the above name contains a large quantity (up to 25 %) of carbonaceous matter. To ensure an accurate estimation of the

total metal it contains, the process used for ordinary ores requires modifying in the manner about to be described.

The Process.

(Time occupied, about 2 hours.)

Weight taken.—Weigh out into a platinum crucible exactly 0·5 of the finely-divided black ore.

Calcining.—Cover the crucible, and place it on a pipe-stem triangle resting upon a tripod; then cautiously heat the crucible by means of a Bunsen burner till the organic matter has burnt off.

Dissolving.—Place the crucible and cover in a 20-oz. beaker containing 50 cc. of nearly boiling strong hydrochloric acid solution, and boil till the whole of the Fe_2O_3 has passed into solution, then wash, and remove the cover and crucible, and quietly evaporate to low bulk, say 10 cc.

Treatment of the solution.—Transfer the liquid without loss to a 10-oz. flask; it is then neutralized, reduced, acidified, titrated, and the percentage of iron is read off exactly as described on p. 235 for the estimation of ores practically free from organic matter.

Determination of Ferrous Oxide in Raw Blackband Ores.

Apparatus required.

Fit up a 120 cc. graduated flask with an india-rubber stopper and valve in the manner described on p. 234.

The Process.

(Time occupied, about 1 hour.)

Weight taken.—Weigh out into the dry flask exactly 0·6 gramme of the finely-divided ore together with a little pure sodium carbonate.

Dissolving.—Add 25 cc. of strong hydrochloric acid, insert the stopper, and cautiously boil the contents of the flask till it is judged that all soluble matter has dissolved.

Diluting.—Next remove the stopper, add 95 cc. of recently-boiled water, loosely replace the stopper, and cool the flask and its contents under the tap: when cold, rinse the stopper and neck of the flask till the wash-water brings the solution to the mark. Close the flask with a plain india-rubber stopper, and thoroughly mix the contents by repeated inversions.

Filtering off the organic matter.—Allow the insoluble matter to settle, and filter off exactly 100 cc. of the solution through a dry 110 mm. filter into a graduated flask. Transfer this without loss, using recently-boiled wash-water, to a 10-oz. flask.

Titration.—This is carried out and the result calculated to FeO exactly as described on p. 236.

Theoretical Considerations.

The foregoing process is not strictly accurate. A little ferrous iron is unavoidably converted during the operations to the ferric state; but on the other hand, it is probable that any organic matter in the solution reduces some of the bichromate, thus possibly producing a compensating

error. The reason for using throughout the analysis recently well-boiled water is, that it is for the time being free from dissolved oxygen, which if present would oxidize the ferrous salt.

ESTIMATION OF TOTAL IRON IN ORES NOT COMPLETELY SOLUBLE IN HYDROCHLORIC ACID.

Re-agent required.

Acid potassium sulphate.—This salt may sometimes be purchased pure and free from water, but to be quite sure of its purity it is best made in the laboratory. It is prepared in the following manner: Introduce into a large porcelain basin 100 grammes of pure powdered potassium nitrate and 60 cc. of pure concentrated sulphuric acid. Place the basin on a tripod, and cautiously heat over a Bunsen, gradually increasing the temperature until no more fumes of nitric acid are evolved, and white fumes of sulphuric acid begin to appear. Allow the liquid sulphate to cool till it begins to solidify, then break up the semisolid mass with a glass rod. When cold, place the acid salt in a large platinum dish, supported on a pipe-stem triangle placed on a tripod, and again quietly fuse the salt, so as to drive off the last traces of water and free sulphuric acid. Be careful, however, not to raise the temperature sufficiently to drive off the combined sulphuric acid. The fused mass is allowed to solidify, and when cold is powdered and preserved for use in a stoppered bottle. It should be pure white in colour.

The Process.

(Time occupied, about 1 hour.)

Weight taken.—Weigh out into a 3-in. platinum dish 0·5 gramme of the finely-divided ore, and intimately mix it with 6 grammes of the powdered acid sulphate.

Fusing.—Heat the covered dish gently over the Bunsen till fusion takes place, and then raise the heat to redness, continuing the fusion for 15 min. The lamp is then removed. When cold, the dish and cover are boiled in a 20-oz. beaker containing 50 cc. of water mixed with 2 or 3 cc. of strong sulphuric acid, till the mass of sulphates is completely dissolved out from the insoluble silica, then wash and remove the cover and dish.

Treatment of the solution.—The acid liquid is transferred without loss to a 10-oz. flask, is neutralized, reduced, acidified, and titrated in accordance with the instructions given on p. 232.

Theory of the Process.

When strongly heated, the acid sulphate gives off free sulphuric acid by the reaction formulated on p. 71. The acid, at the comparatively high temperature of the fusion, readily attacks the oxides of iron present, thus—

$$FeO + H_2SO_4 = FeSO_4 + H_2O$$

$$Fe_2O_3 + 3\ H_2SO_4 = Fe_2(SO_4)_3 + 3\ H_2O$$

The ferrous and ferric sulphates, together with the co-produced normal potassium sulphate, readily dissolve in the acidulated water. The SiO_2 is left insoluble, but the other bases pass into solution as $MnSO_4$, $Al_2(SO_4)_3$, $CaSO_4$, $MgSO_4$, etc.

Estimation of *FeO* in Insoluble Ores.

Apparatus required.

Fit up the apparatus sketched in Fig. 18: A is a perfectly

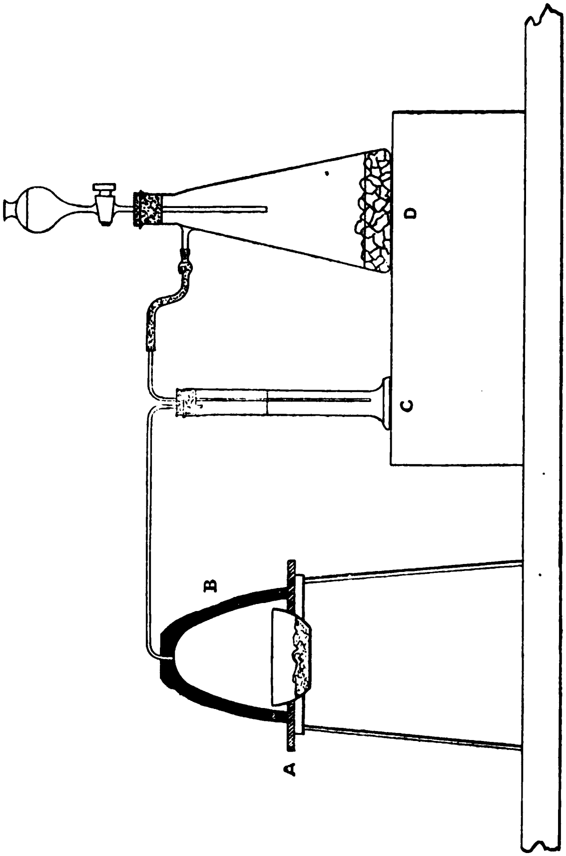


FIG. 18.

flat fire-clay plate 6″ sq. × ¼″ thick, and perforated in the

centre with a hole $2\frac{1}{2}''$ in diameter. In this rests a covered $3''$ platinum dish, over which is inverted a sufficiently large fire-clay crucible, B, in the bottom of which a hole has been drilled, into which has been cemented a bent glass tube $\frac{1}{8}''$ inside diameter. The cement with which to fix this in is made by kneading to a very stiff dough a little finely-ground ganister with thick liquid silicate of soda. On leaving the fitted crucible for a few hours on the hot plate, the cement sets harder than the burnt fire-clay itself.

The Process.

(Time occupied, about 2 hours.)

Weight taken.—Intimately mix 0·5 gramme of the ore with 6 grammes of acid potassium sulphate, as in the process last described. Place the covered crucible in the hole of the perforated plate, and support the latter on a tripod. The fire-clay crucible is then inverted over the dish, and the glass bend is connected with an apparatus evolving CO_2 washed by passing it through a cylinder of water. Fig. 18 C is a washing cylinder; D a filter-pump vessel containing marble and water, into which hydrochloric acid is delivered as required from a separator. Pass the gas for several minutes, till it is judged that the air in the dish and its vicinity is expelled, then, very cautiously at first, heat the bottom of the dish with a Bunsen burner for the same length of time as that occupied in the fusion for estimating the total iron; then take away the lamp, and allow the dish and its contents to cool in the current of CO_2.

Dissolving—The fused mass is extracted in a covered beaker by heating with dilute sulphuric acid, the cover

and crucible are rinsed with recently-boiled water, and are then removed.

Titration—Next, without loss of time, the acid solution is titrated in the beaker with the standard bichromate solution, and the cc. required are converted to FeO by multiplying them by 1·2857.

Theoretical Considerations.

The result obtained by the foregoing process is only approximate, being always somewhat low from a slight oxidation of the $FeSO_4$ to $Fe_2(SO_4)_3$ by the action of the air, the — error being of course increased if peroxide of manganese was originally present for the reason specified on p. 233. The object of carrying out the fusion in an atmosphere of CO_2 is of course to reduce the atmospheric oxidation to a minimum.

Estimation of Manganese in soluble Inorganic Ores.

(Time occupied, about 3 hours.)

Weight taken.—Weigh out into a 20-oz. beaker 6 grammes of the dry, pulverized ore.

Dissolving.—Heat and cautiously boil in a covered beaker with about 60 cc. strong HCl till the residue is fairly white.

Fractional filtration.—Transfer the solution and residue without loss to a 60 cc. flask. When cold, dilute to the mark, thoroughly mix, and through a dry 110 mm. filter receive 50 cc. of the liquid, corresponding to 5 grammes of ore, into a dry, graduated flask. (If there is a very large

silicious residue, its volume may be allowed for by making the original bulk 60·5 instead of 60 cc.)

Converting the iron and manganese into nitrates.—Transfer the 50 cc. of solution without loss to a 20-oz. beaker. Boil down to about 10 cc., add 50 cc. strong nitric acid, and boil down to 30 cc. to expel HCl.

Remaining operations.—The manganese is then determined by the volumetric process described on p. 84 *et seq.*, the solution obtained in the last paragraph being treated in exactly the same manner as the nitric acid solution of 5 grammes of steel.

Calculation of result.—The result is obtained in terms of percentage of metallic manganese. This multiplied by $1·582 = MnO_2$, or by $1·291 = MnO$.

Example.—A sample of hematite treated by the foregoing process required in the titration 89 cc. of the standard bichromate solution to oxidize the excess of ferrous iron; then $100 - 89 = 11$, and $11 \times ·02 = 0·22$ Mn, and $0·22 \times 1·582 = 0·35\,\%$ MnO_2.

Gravimetric Method.

(Time occupied, about ¾ day.)

Weight taken.—Weigh out 2·88 grammes of the ore into a 20-oz. covered beaker.

Dissolving.—Digest with 50 cc. strong HCl till the residue is nearly white; then oxidize any ferrous iron by boiling for a minute or two with 2 cc. strong nitric acid.

Remaining operations.—Make up when cold to from 60 to 60·5 cc., according to the amount of silicic residue present. Filter off 50 cc., and treat the solution thus obtained containing 2·4 grammes of ore exactly according to the

process described for the gravimetric estimation of manganese in steel. The result may be a little high, owing to the final residue of Mn_3O_4 containing traces of Al_2O_3, ZnO, and $BaSO_4$.

Estimation of Manganese in Organic Ores.

In black-band ores 2·88 grammes of the ore are dissolved in HCl after a previous calcination as described on p. 237. The remaining operations are identical with those just described.

Determination of Manganese in Insoluble Ores.

The manganese in iron ores insoluble in HCl is estimated by fusing 2·88 grammes with acid potassium sulphate. The mass is extracted in dilute HCl; when cold, the solution is made up to known bulk, five-sixths are filtered off, and the estimation is proceeded with by the acetate process as usual, the result being calculated on 2 grammes.

Determination of Crude Silica.

(Time occupied, about 3 hours.)

Weight taken.—Weigh out 2 grammes of the finely-divided ore into a 20-oz. covered beaker.

Dissolving.—Add 40 cc. strong HCl, boil cautiously, and eventually quietly evaporate to complete dryness with the cover off.

Remaining operations.—The dry mass is re-dissolved in HCl, and the insoluble residue is estimated exactly in the

manner described for the determination of silicon in steel on p. 67.[1]

Example.—Analysis of Rubio brown hematite. Weight taken, 2 grammes of ore dried at 100° C.

$$\begin{array}{rl} \text{Weight of crucible + residue} = & 27{\cdot}9338 \\ \text{Weight of crucible} = & 27{\cdot}6309 \\ \hline & {\cdot}3029 \text{ gramme } SiO_2. \end{array}$$

$$\frac{{\cdot}3029 \times 100}{2} = 15{\cdot}14\,\%$$

Estimation of P_2O_5 in Non-Arsenical Ores.

Weight taken.—The amount of ore weighed out and the process to be used must be decided after reading the remarks and inspecting the table on p. 190.

Dissolving.—The ore is dissolved by boiling with strong HCl. The solution is evaporated to complete dryness, the mass is taken up in strong HCl, made up when cold to 60 cc., and $\frac{5}{6}$ths of the solution is filtered off.[2]

Remaining operations.—The liquid obtained as above is then—

(*a*) Diluted, reduced, and the phosphoric acid is determined by the "combined method" described for steel on p. 123; or

(*b*) It is evaporated to low bulk, and estimated by the rapid process described for steel on p. 111.

The pyrophosphate contains ·63·79, and the yellow precipitate 3·73 % of P_2O_5.

[1] When it is necessary to obtain the silica quite free from impurities, it must be fused and obtained pure by the process given for ganister on p. 275.

[2] In the case of ores containing titanic acid, it is essential to examine the washed insoluble residues for phosphoric acid, which, if present, is estimated by the method given for titanic pig-irons on p. 198.

Examples.

Analysis of Dannemora magnetite.

Weight of dry ore taken 12 grammes.
Weight of dish + yellow ppt. = 33·6295
Weight of dish = 33·6122

·0173

$$\frac{\cdot 0173 \times 3\cdot 7}{10} = 0\cdot 006 \% \ P\,O_5.$$

Analysis of Northampton brown hematite.

Weight of raw dry ore taken 1·2 grammes.
Weight of crucible + $Mg_2P_2O_7$ = 27·9324
Weight of crucible = 27·9006

·0318 gramme $Mg_2P_2O_7$
Correction for solubility + ·0010

·0328

$$\frac{\cdot 0328 \times 63\cdot 79}{1} = 2\cdot 09 \% \ P_2O_5.$$

Estimation of Arsenic and P_2O_5.

Weigh out 6 grammes of the finely-divided ore into a 20-oz. covered beaker, add 10 cc. strong nitric acid, and to avoid bumping, heat on a pipe-stem triangle. When the evolution of any CO_2 has ceased the cover is removed, and the contents of the beaker are quietly evaporated to complete dryness, the mass being heated in the centre of the hot plate till any nitrates formed are decomposed. The soluble portion of the dry mass is then dissolved at the lowest possible temperature in 40 cc. of HCl; 50 cc. of the clear solution, corresponding to 5 grammes of ore, are separated in the usual manner by fraction filtration. The liquid is then diluted, neutralized, reduced with H_2SO_3, and the phosphoric acid and arsenic are determined exactly as described on p. 128. In the present case, the preliminary treatment with the nitric acid has for its

object the oxidation of any arsenic existing as sulphide to arsenic acid, As_2O_5.

Determination of Sulphur.

Sulphur is estimated by the *aqua regia* method described for steel on p. 96.

Examination of the insoluble residue.—When absolute accuracy is required the washed insoluble residue is fused with 6 grammes of the fusion mixture specified on p. 138. The fusion is extracted with hot water, made up when cold to as small a definite volume as possible, five-sixths of the clear liquid is filtered off, acidified with HCl, and evaporated to dryness; the dry mass is taken up in HCl and water, the SiO_2 is filtered off, washed, and the SO_3 is precipitated by boiling the filtrate after evaporating to 100 cc. by addition of $BaCl_2$. The resulting $BaSO_4$ is estimated as usual, and the percentage of sulphur contained therein is added to the main quantity. This examination of the insoluble residue is more particularly necessary in the case of ores containing barium, because in such the residue is very liable to contain $BaSO_4$, which the fusion converts into insoluble BaO and Na_2SO_4 soluble in water. In the foregoing process a blank estimation of the sulphur in the fusion mixture is of course made, and the $BaSO_4$ obtained deducted.

Determination of Alumina.

(Time occupied, about 1 day.)

Weight taken.—Weigh out 1·44 grammes of ore into a 20-oz. covered beaker.

Dissolving and separating the SiO_2.—Dissolve in 30 cc. of strong HCl, evaporate to dryness, take up in 20 cc. of HCl, and obtain 50 cc. of clear solution containing 1·2 grammes of ore by fractional filtration.

Remaining operations.—The yellow liquid is transferred without loss to a 30-oz. registered flask, 3 cc. of the standard solution of sodium phosphate specified on p. 167 are added, the solution is diluted to 200 cc., neutralized with dilute ammonia, reduced with H_2SO_3, precipitated with ammonium acetate, and the alumina is determined in exact accordance with the instructions given on p. 168 *et seq.*[1] for the estimation of aluminium in steel. The ignited precipitate contains 41·85 % of Al_2O_3. The foregoing process gives only the soluble alumina present in the ore: when great accuracy is required the insoluble residue must be analyzed by the process described on p. 259, and any alumina contained therein be added to the main quantity. In ores containing soluble titanic acid or chromic oxide, the aluminium phosphate will be more or less contaminated with these substances.

Example.

A sample of Yorkshire clay ironstone gave on analysis the following result:—

Weight taken 1·44 grammes.

$$\begin{aligned} \text{Weight of crucible} + AlPO_4 &= 32{\cdot}3962 \\ \text{Weight of crucible} &= 32{\cdot}2816 \\ \hline &\ \ \ \cdot 1146 \text{ gramme } AlPO_4. \end{aligned}$$

$$\frac{\cdot 1146 \times 41{\cdot}85}{1} = 4{\cdot}8\ \%\ Al_2O_3.$$

[1] It is also advisable to re-precipitate the phosphate before weighing in the manner described for ferro-aluminium on p. 218.

DETERMINATION OF LIME AND MAGNESIA.

(Time occupied, about 1½ days.)

Weight taken.—Weigh out into a 20-oz. beaker 1·2 grammes of the finely-divided ore, or in the case of a carbonate 2·4 grammes should be employed.

Dissolving.—Add 40 cc. strong *HCl*, boil down on the hot plate, add 2 cc. strong nitric acid, and then evaporate the contents of the beaker to complete dryness with the cover off. When cool, the mass is re-dissolved in about 30 cc. strong *HCl*, and the solution is quietly evaporated down to about 10 cc.

Fractional filtration.—The solution and residue are transferred without loss to a 60 cc. graduated flask, and the liquid when cold is made up to the mark, well mixed, and 50 cc., corresponding to 1 gramme of ore, are filtered off through a dry paper into a graduated flask.[1]

First precipitation of Fe_2O_3 *and* Al_2O_3.—The 50 cc. of solution are transferred to a 20-oz. beaker, and diluted with warm water to about 200 cc. Next add, little by little, with constant stirring, dilute ammonia, till the liquid is faintly alkaline. The solution is then boiled, and is finally digested for a few minutes on the corner of the plate.

First filtration.—The precipitate is collected on a well-fitting, thick German filter-paper, contained in a 3-in. funnel, the paper having been previously well washed with hot *HCl* and water. The filtrate is collected in a clean 20-oz. beaker. The precipitation beaker is well rinsed out,

[1] The insoluble residue may be fused and tested for lime and magnesia, but as a rule it will be found to be practically free from these oxides.

and the precipitate is slightly washed with hot water, and allowed to drain well; the clear filtrate is then put on a hot plate to concentrate by evaporation.

Re-dissolving.—The funnel is supported on a hanger inside the beaker in which the precipitation took place, and the hydrates (and phosphates) of iron and aluminium are re-dissolved in moderately strong hot HCl. The paper having been washed free from iron alternately with hot acid and cold water, is put aside under cover till required for the second filtration.

Second precipitation and filtration.—The yellow solution is boiled down in the covered beaker to 5 cc. It is then diluted and precipitated with dilute ammonia exactly as before. The precipitate is collected on the previously used paper, and washed with hot water, the filtrate being received in a beaker containing the concentrated first filtrate. The double filtrate is then boiled down in a covered beaker to about 150 cc.

Separating the manganese and nickel.—Add to the liquid 10 cc. of dilute ammonia, and pass a current of washed H_2S through the boiling liquid for some minutes, to precipitate as sulphide any manganese and nickel not carried down with the iron and aluminium. The sulphides are allowed to settle, are filtered off, and washed with water containing a little ammonia and H_2S solution, the filtrate and washings being collected in a clean 20-oz. beaker. The latter is then covered, and its contents are brought to boiling. (In ores containing only small percentages of manganese the foregoing precipitation may be omitted, because when only a few tenths per cent. are present the manganese is all carried down as hydrate with the iron and alumina.)

Precipitating the CaO.—Next add to the boiling fluid down the lip of the beaker 10 cc. of a saturated solution

of ammonium oxalate, and sufficient dilute ammonia to make the liquid distinctly alkaline. Boil for fifteen minutes, digest for at least an hour, remove the beaker from the plate, and allow the precipitated oxalate of calcium to settle thoroughly.

Filtering off and weighing the CaO.—The precipitate is collected on a 110 mm. paper contained in a 2¼-in. plain funnel, the filtrate containing the magnesia being received into a clean 20-oz. beaker. The precipitate and paper must be thoroughly washed with hot water; they are then dried, strongly ignited in a tared platinum crucible, which when cold is quickly re-weighed, the residue of CaO being very hygroscopic.[1]

Estimating the magnesia.—To the filtrate and washings from the lime add 50 cc. strong nitric acid, and gently boil and evaporate the contents of the covered beaker down to low bulk, say 5 cc. Next add 5 cc. of a 10 % solution of ammonium or ordinary sodium phosphate and 2 cc. of HCl, and then cautiously dilute ammonia in slight excess. The volume of the liquid is then made up to 50 cc. with strong ammonia solution; the liquid is allowed to stand for some hours, being occasionally briskly shaken round. The precipitate is collected on a 90 mm. pure paper, and is washed, dried, ignited, and weighed as $Mg_2P_2O_7$ in exact accordance with the instructions given on p. 122. The residue contains 36·2 % MgO.

[1] As a check the CaO may be converted into $CaSO_4$ by adding to the crucible 1 cc. of dilute sulphuric acid, evaporating to dryness, gently igniting, and when cold re-weighing. The precipitate contains 41·2 °/。 CaO.

Example.

Sample of Ulverston red hematite.

Weight taken 1·2 grammes.

Lime. Weight of crucible + CaO = 27·3962
Weight of crucible = 27·3846

·0116 gramme CaO.

$$\frac{\cdot 0116 \times 100}{1} = 1\cdot 16\ \%\ CaO.$$

Magnesia. Practically absent = Trace MgO.

Theoretical Considerations.

The filtrate from the insoluble residue contains ferric, aluminic, calcic, magnesic, and manganous chlorides, and if present, cupric and nickelous chlorides; the whole of the phosphoric acid is also in solution. If present, there will likewise be dissolved in the liquid a portion of the titanic acid, and possibly chromic chloride, but only traces of arsenic acid, most of the latter having been volatilized as chloride. The solution is evaporated to low bulk to avoid the presence in the filtrate of an unwieldy excess of $AmCl$ in the final evaporation to low bulk to determine the magnesia. On precipitation with ammonia the hydrates of ferric iron and aluminium carry down with them the whole of the P_2O_5, TiO_2, and Cr_2O_3 which may happen to be in solution. Also, the hydrates of nickel, manganese, and copper may be wholly or partially carried down. Unfortunately small portions of the lime and magnesia are also precipitated, hence the necessity for a second separation. The $AmCl$ in the filtrate containing the lime and magnesia retains the latter in solution as a soluble double chloride $AmMgCl_2$, whilst on the addition of ammonium oxalate the calcium is precipitated thus—

$Am_2C_2O_4 + CaCl_2 = CaC_2O_4 + 2\ AmCl$. Ammonium oxalate and calcic chloride yield white insoluble calcium oxalate and ammonium chloride. On strongly igniting the oxalate of lime decomposes thus—$CaC_2O_4 = CaO + CO_2 + CO$. Calcium oxalate yields caustic lime, carbonic oxide, and carbonic acid gases. The lime readily absorbs moisture to form a hydrate, thus—$CaO + H_2O = Ca(HO)_2$. On evaporating the filtrate from the lime with strong nitric acid, the somewhat large amount of $AmCl$ necessarily present for ensuring the separation of the lime and magnesia is decomposed into ammonium nitrate, and the latter as the evaporation proceeds is volatilized as water and laughing gas N_2O. The operation of precipitating the magnesia with phosphoric acid is the converse of that theoretically considered on p. 125. It is necessary to separate manganese and nickel, otherwise both the lime and magnesia precipitated are respectively liable to be contaminated with the oxides or phosphates of these metals. The introduction of bromine into the foregoing analysis is dangerous, because on evaporating down the filtrate from the lime with nitric acid the ammonium bromide is decomposed into a mixture of bromine and hydrobromic acid, which attacks the glass of the beaker, throwing silica and the bases in the glass into solution, and consequently making the result of the MgO estimation seriously high.

If bromine could be safely employed the precipitation of the whole of the manganese with the iron could be readily ensured, rendering the sulphide precipitation unnecessary.

Determination of CO_2.

(Time occupied, about 2 hours.)

Weight taken.—In the case of oxides, 5 grammes should be employed for the estimation. When a raw carbonate is under examination 0·5 gramme of the finely-divided ore is weighed out into a dry 8-oz. wide-mouthed flask.

Remaining operations.—The flask is attached to the apparatus sketched in Fig. 7, in the manner described in the process for the estimation of carbon in steel by moist combustion. A current of air having been aspirated through the apparatus, the weighed absorption tubes are attached, and, whilst continuously maintaining a gentle flow of air, 50 cc. of dilute sulphuric acid, 1 in 3, are gradually admitted from the stoppered funnel. For a few minutes the action should be continued in the cold, but afterwards a gentle heat is applied to the sand-bath till no further evolution of CO_2 takes place. Every trace of CO_2 is then swept forward to the absorption tubes by the aspiration of at least a litre of air. The increase of weight in the potash bulbs and chloride of calcium tube is then determined in the manner described for the estimation of carbon in steel by combustion, described on p. 36.

Precaution.—It is absolutely essential to avoid any back pressure from the flask into the purifying tube containing the potash pumice.

Example.

Analysis of uncalcined Derby ore (Staveley).

Weight taken 0·5 gramme.

Weight of absorption tubes before evolution.

$$KHO = 32{\cdot}6934$$
$$CaCl_2 = 58{\cdot}1754$$
$$\overline{90{\cdot}8688}$$

Weight of absorption tubes after evolution.

$$KHO = 32{\cdot}8202$$
$$CaCl_2 = 58{\cdot}2002$$
$$\overline{91{\cdot}0204}$$
$$90{\cdot}8688$$
$$\overline{{\cdot}1516 \text{ gramme } CO_2}$$

$$\frac{{\cdot}1516 \times 100}{0{\cdot}5} = 30{\cdot}32\ \%\ CO_2$$

or briefly, $15{\cdot}16 \times 2 = 30{\cdot}32\ \%\ CO_2$ as before.

Estimation of Combined Water and Organic Carbon.

These are determined by strongly combusting in oxygen 1 gramme of the very finely-divided ore contained in a porcelain boat, placed in a combustion tube containing the usual column of recently-ignited CuO scales in the apparatus sketched in Fig. 7. The potash pumice tube is, however, replaced by a bulb containing strong sulphuric acid, and between the combustion tube and the chromic acid bulb is also placed a weighed bulb containing strong H_2SO_4.[1] The first-named bulb serves to dry the oxygen; the second, to absorb the water formed. The apparatus having been connected up, a current of air is aspirated through to remove any condensed moisture in the tube. The three absorption tubes are then carefully weighed with the usual precautions, replaced, and the combustion

[1] The limb of this bulb must be inserted direct into the india-rubber bung of the combustion tube.

is made exactly as described on p. 34 *et seq.*, for the estimation of carbon in steel. The final aspiration must, however, be continued until every trace of moisture has been carried forward into the H_2SO_4 bulb. The increase in the sulphuric acid bulb represents the total combined water, which is due not only to inorganic hydrate, but also to that existing in any organic matter present in the ore.[1] The organic water in pure hematites and magnetites is very small. In black-band ores the water obtained will be largely of organic origin. The increase in the potash and chloride of calcium tubes represents the inorganic CO_2 (driven off by heat from its combination with the oxides in the ore), augmented by the carbon of the organic matter (burnt by the oxygen). The weight of CO_2 obtained by evolution in the manner described in the last article is deducted from the total weight, and the remainder multiplied by 27·27 gives the weight of organic carbon.

Example.

Analysis of a sample of Northamptonshire brown hematite.

Weight taken 1 gramme.

Increase in H_2SO_4 bulb 0·1167 = 11·67 °/ₒ of total combined H_2O.

$$\left.\begin{array}{r} \text{Increase in } KHO \text{ and } CaCl_2 \text{ bulbs} = 0{\cdot}6264 \\ \text{Less weight of } CO_2 \text{ obtained by evolution} = 0{\cdot}5956 \end{array}\right\} \text{gramme.}$$

$$\cdot0308 \text{ organic } CO_2.$$

$\cdot0308 \times 27{\cdot}27 = 0{\cdot}84$ °/ₒ organic carbon.[2]

[1] See footnote to "organic carbon."

[2] The percentage of organic carbon multiplied by 60 and divided by 40 gives the approximate percentage of organic matter, the difference between the "carbon" and "matter" being organic water, which may be deducted from the total water to obtain the water of hydration in the ore.

Estimation of Copper.

Dissolve 12 grammes of the ore in a mixture of 30 cc. of aqua regia and 30 cc. strong HCl, evaporate to dryness, take up in about 50 cc. of HCl, evaporate to 10 cc., and obtain 100 cc. of clear solution, corresponding to 10 grammes of ore, by fractional filtration. The liquid is transferred to a 30-oz. registered flask, neutralized with ammonia, reduced with sulphurous acid, and the copper is precipitated in a volume of 300 cc. by means of a current of washed H_2S passed for about ten minutes through the hot solution. The precipitated CuS is filtered off, and the copper determined exactly in the manner described on p. 178 *et seq.*

Estimation of Nickel.

Obtain 10 grammes of the ore in 100 cc. clear HCl solution in the manner just described for copper. The liquid is transferred to a 30-oz. registered flask, neutralized with pure sodic hydrate, reduced with sulphurous acid, and the nickel is precipitated in an acetic acid solution by means of H_2S and pure sodic acetate. The percentage of nickel is determined exactly as described for its estimation in steel on p. 161 *et seq.* If copper is present, the instructions on p. 164 are also followed.

Estimation of Cr_2O_3.

Some ores of iron, such as those from the Tasmanian mines, contain about 3 % of Cr_2O_3. The latter may be estimated as phosphate by the process described for steels containing aluminium on p. 150. The precipitate contains 60·95 % of Cr_2O_3.

Estimation of Titanic Acid.

Six grammes of the ore are dissolved in a 20-oz. beaker in about 60 cc. *HCl*, 10 cc. of a 10 % solution of ammonium phosphate are added, the liquid is evaporated to complete dryness, and strongly heated in the centre of the plate. The dry mass is taken up in *HCl*, the insoluble residue filtered off, washed, and the TiO_2 therein is determined in the manner described on p. 196 for the estimation of *Ti* in pig-iron.

Determination of the Alkalies.

Potash, K_2O, and soda, Na_2O, when present in ores of iron, seem to be almost entirely found in the residue insoluble in *HCl*, probably in the form of the insoluble silicates orthoclase ($Al_2K_2Si_3O_8$) and albite ($Na_2Al_2Si_6O_{16}$). The residue is therefore examined for alkalies by the method described for their estimation in fire-clay (p. 283).

Analysis of the Insoluble Residue.

One gramme of the ignited residue is thoroughly fused with 10 grammes of a mixture of K_2CO_3 and Na_2CO_3; the fusion is extracted, and the SiO_2, Al_2O_3, CaO, MgO, and FeO present are estimated as described for fire-clay on pp. 280-1. The last-named oxide when present, as is usual, in minute quantity, is estimated colorimetrically.

ANALYSIS OF MANGANESE ORES.

Determination of CaO and MgO.—As a rule, the methods given for the estimation of the various con-

stituents of iron ores are also available for manganese ores. In determining lime and magnesia, however, it is advisable to originally weigh out 1·44 grammes, and after precipitating the MnS in the manner described on p. 251, to make up the solution and precipitate to 301 cc., filter off 250 cc. of clear liquid, corresponding to 1 gramme of ore, and so avoid the troublesome washing of the somewhat bulky precipitate. The lime and magnesia are then determined in the fractional filtrate by the processes given for iron ores.

Determination of Total Manganese.

Gravimetric method.—The manganese may be estimated by the gravimetric acetate process, but the results are liable to be high, owing to the final precipitate of Mn_3O_4 containing oxide of zinc or sulphate of barium, which are not infrequent constituents of manganiferous ores.

Volumetric Process.

(Time occupied, about 2 hours.)

Weight taken.—Weigh out into a 20-oz. covered beaker from ·25 to 0·5 gramme of the finely-pulverized ore, dried at 100° C. In the case of rich ores, in which the weight first named is employed, 0·5 gramme of Swedish bar-iron is also weighed out.

Remaining operations.—These are carried out respectively by the processes described for the assay of ferromanganese on p. 204 and spiegel on p. 202 by Pattinson's method.

ESTIMATION OF MnO_2 (BUNSEN) (AND MnO BY DIFFERENCE).

(Time occupied, about 1 hour.)

Re-agents required.

Standard solution of sodium thiosulphate.—Prepared by dissolving 27·091 grammes of hypo in a litre of water in the manner described on p. 175.

10 % *solution of KI.*—Dissolving 10 grammes of pure potassic iodide crystals in 100 cc. of water.

The Process.

Weight taken.—Weigh out into a clean, dry 6-oz. flask exactly 0·25 gramme of the finely-pulverized dry ore.

Apparatus required.—The flask is then fitted with an india-rubber stopper[1] carrying a stoppered funnel and exit bend, and is attached to the absorption cylinder sketched in Fig. 12.[2] The cylinder is charged with 70 cc. of the 10 % solution of pure potassic iodide in distilled water, and is attached to an aspirator.

Dissolving.—Add from the stoppered funnel 20 cc. of strong HCl (proved to be devoid of free chlorine). Place the flask on the edge of the hot plate, and gently heat till the ore has decomposed, maintaining meanwhile a slight pull through the cylinder containing the KI by means of

[1] This must be freed from surface by well boiling with dilute sodic hydrate solution, and afterwards in several changes of water.

[2] The exit tube from the flask should touch the inlet tube to the cylinder, the two being joined with a short piece of sound india-rubber tubing so as to avoid any absorption of Cl by the material last named.

the aspirator. The current of gas, however, should be as slow as possible. When the ore has dissolved, the tap of the funnel is partially opened, and every trace of chlorine in the flask is swept forward into the cylinder by the slow aspiration of at least half a litre of air, the acid in the flask being maintained just short of boiling-point.

Titrating the liberated iodine.—The cylinder is detached from the apparatus, the india-rubber stopper removed, and the inlet tube and bulb are rinsed inside and out with distilled water. The yellowish-brown liquid containing the iodine is then poured into a 20-oz. beaker, the cylinder being well rinsed out, and the washings added to the main quantity of solution. The titration is then made by running in from a burette the standard solution of thiosulphate, till the colour due to the iodine is nearly discharged, when 2 cc. of a filtered solution of starch are added, and the titration is completed in the manner described on p. 176. Each cc. of hypo required corresponds to 1 % of metallic manganese existing in the ore as MnO_2. The result deducted from the total manganese obtained by the process described in the last article gives the amount of manganese existing as MnO. These two percentages multiplied respectively by 1·5818 and 1·2909 give the respective proportions of dioxide and monoxide present.

Example.

Total manganese 20·8 % (existing as ($x\ MnO_2 + y\ MnO$)).
cc. of hypo required 19·2 = 19·2 % of Mn existing as MnO_2.
$\overline{1·6}$ = $\overline{1·6}$ % of Mn existing as MnO.

19·2 × 1·5818 = 30·37 % MnO_2.
1·6 × 1·2909 = 2·06 % MnO.

Theoretical Considerations.

The manganese dioxide in the ore evolves free chlorine from the HCl, thus—

$$MnO_2 + 4\ HCl = 2\ Cl + MnCl_2 + 2\ H_2O$$

Seventy-one parts by weight of chlorine correspond to 55 parts of metallic manganese existing as peroxide. The evolved chlorine liberates iodine from the solution of potassic iodide (the iodine remaining dissolved in the excess of the latter present), thus—

$$2\ KI + 2\ Cl = 2\ KCl + 2\ I$$

Therefore, 254 parts by weight of iodine are equivalent to 55 parts of manganese existing as dioxide.[1] The results obtained are liable to be low in the presence of organic matter and of ferrous oxide (see p. 233), owing to the conversion of some of the liberated chlorine into HCl by the action of such readily oxidized substances.

ESTIMATION OF MnO_2 BY PATTINSON'S METHOD.

(Time occupied, about 1 hour.)

Cut off by means of a small, sharp saw-file a half-inch test tube 1 in. from the bottom, and carefully fuse the cut edge in the blow-pipe flame.

Weight taken.—Weigh out into the short test tube 0·25 gramme of the dry ore previously reduced to an impalpable flour in the agate mortar; also weigh out 0·51 gramme of standard Swedish iron into a dry, wide-mouthed 20-oz. flask.

Dissolving.—Add to the iron a mixture of 25 cc. of strong sulphuric acid and 75 cc. of water. Cover the

[1] See theoretical notes on p. 183.

flask with a watch-glass, and boil the acid till the last trace of iron has dissolved; rinse and remove the watch-glass. The flask is then inclined till nearly horizontal, and by means of a pair of forceps the little tube containing the manganese ore is carefully slid down the neck into the acid solution of ferrous sulphate. The flask is re-covered, and its contents are boiled till the ore has dissolved. The vessel is then removed from the plate, the watch-glass and sides of the flask are rinsed, and the contents are diluted to 200 cc. with recently-boiled distilled water.

Titrating.—The excess of ferrous sulphate is then determined exactly as described for the assay of ferro-manganese on p. 204: the number of cc. used subtracted from 50 and multiplied by 2 gives the percentage of manganese existing as MnO_2. This deducted from the total manganese gives the percentage of metal existing as MnO; the respective percentages of the two oxides are calculated by the multipliers given in the last article. If any ferrous oxide was originally present in the ore, the indicated MnO_2 is below the truth, the MnO result being, of course, correspondingly high.

ANALYSIS OF CHROME IRON ORE OR CHROMITE.

In addition to being smelted in the blast-furnace for the production of chrome pig, this product is now extensively used for isolating the basic (CaO, MgO) beds of open-hearth furnaces from the acid (SiO_2) walls and roof. It consists essentially of a mixture of Cr_2O_3, MgO, Al_2O_3, FeO,[1] together with smaller percentages of CaO and SiO_2.

[1] In reporting the analysis the iron is usually calculated to FeO, but occasionally notable quantities of the iron present may exist in the form of Fe_2O_3.

Estimation of Cr_2O_3.

(Time occupied, about 1 day.)

Weight taken.—Weigh out 0·6 gramme of the ore, *reduced to the finest possible state of division in the agate mortar,* into a deep 3-in. platinum dish.

Fusing with $HKSO_4$.—Intimately mix the ore with 6 grammes of powdered pure acid potassium sulphate, cover the dish, and gradually fuse the mass over a Bunsen, the dish being placed on a pipe-stem triangle supported on a tripod. The sulphate is kept liquid at a gentle heat for half-an-hour, when the flame is increased, till most of the white fumes of free sulphuric acid have volatilized. The dish and its contents are then allowed to cool.

Second fusion.—Remove the cover, and spread on the surface of the fused cake 20 grammes of the fusion mixture specified on p. 138. The cover is replaced, and the whole mass is fused, quietly at first, and maintained in a liquid condition for half-an-hour, when it is allowed to cool.

Extracting and precipitating the Cr as hydrate.—These operations are identical with those described on p. 140 *et seq.* The precipitate corresponding to 0·5 gramme of ore is collected on a 125 mm. pure paper contained in a 3-in. funnel. The hydrate is re-dissolved in the smallest possible quantity of hot dilute sulphuric acid, 1 in 4, the solution being received into a 30-oz. registered flask, together with the liquid resulting from an exhaustive washing of the filter-paper with dilute acid and water.

Oxidizing and titrating the Cr.—The sulphuric acid solution is then diluted, oxidized with potassic permanganate, the resulting precipitate dissolved in strong HCl, and

after boiling off the chlorine, the chromium in the rich yellow liquid is estimated exactly as for ferro-chrome on p. 209. The percentage of Cr obtained multiplied by 1·46 gives the percentage of Cr_2O_3.

Theoretical Considerations.

The preliminary fusion with $HKSO_4$ converts the whole of the bases present into sulphates. In the subsequent alkaline fusion the chromic sulphate (together with any traces of undissolved Cr_2O_3) is oxidized to alkaline chromate.

Estimation of SiO_2.

(Time occupied, about 1 day.)

Weight taken and fused.—One gramme of the floured ore is fused in a deep platinum dish with the usual precautions with 15 grammes of pure powdered acid potassium sulphate.

Extracting the fusion.—This is effected by boiling the dish and cover in a 20-oz. covered beaker with 80 cc. of water and 20 cc. strong HCl. When clean, the cover and dish are washed and removed, the liquid is then well boiled in the covered beaker.

Fusing the residue.—The insoluble residue is next collected without loss on a 90 mm. pure filter, is well washed with hot water, dried, and ignited in a platinum crucible. When cold, the ignited residue is mixed in the crucible with 3 grammes of the fusion mixture specified on p. 138, and is then fused for half-an-hour in the usual manner.

Second extraction.—When cold, the fusion is extracted in about 30 cc. of hot water contained in a deep 4-in. basin heated on the water-bath; when clean, the crucible and cover are washed and removed.

Precipitating and weighing the SiO_2.—The basin is covered with a clock-glass, and 20 cc. of strong HCl are poured down the lip. When the evolution of CO_2 has ceased, the cover is rinsed and removed, and the contents of the basin are evaporated to complete dryness. The mass is then drenched with 10 cc. of strong HCl, is again taken to dryness, and moistened with 10 cc. of acid; 50 cc. of water are added, and when, after heating a few minutes, the chlorides have completely dissolved, the silica is collected on a 90 mm. pure paper, is well washed with hot dilute HCl and water, being dried, ignited, and weighed in the usual manner. The weight obtained, multiplied by $100 = \%\ SiO_2$.

Theoretical Considerations.

The fusion with the acid sulphate converts the bulk of the bases into soluble sulphates, which are removed in the first extraction, leaving insoluble SiO_2 together, usually with a little undecomposed ore. The latter is disintegrated on the second fusion, and by the double evaporation with HCl the bases are converted into soluble chlorides, and insoluble SiO_2 is precipitated. The extraction of the alkaline fusion is made in porcelain, because the fluid is liable to take up SiO_2 from a glass beaker.

Estimation of the Magnesic, Aluminic, and Ferrous Oxides.

(Time occupied, about 1½ days.)

Preliminary operations.—Fuse 0·5 gramme of the floured ore, first with $HKSO_4$, and then with the alkaline fusion mixture, and extract the fusion exactly as described for the estimation of Cr_2O_3 on p. 265. The whole of the residue is, however, collected on a 90 mm. pure paper, being well but cautiously washed round the edges of the filter with hot water. It is then dried till required later on. The filtrate and washings must be collected in a clean 20-oz. beaker.

Recovery of the soluble Al_2O_3.—The yellow filtrate containing the chromate is heated nearly to boiling, removed from the plate, and is mixed with 10 cc. of a saturated solution of re-sublimed ammonium carbonate. A current of washed CO_2 is then passed through the hot liquid for about half-an-hour. The precipitated basic carbonate of alumina is allowed to settle somewhat, filtered off on a 90 mm. pure paper, cautiously washed with hot water till free from chromate, and is then dried.

Estimating the MgO.—The two filter-papers are ignited in a platinum crucible: when cold, the residue is carefully brushed out into a 20-oz. beaker. A few cc. of HCl are boiled in the crucible and washed out upon the residue, to which a further quantity of about 25 cc. of HCl is added. The contents of the beaker are then briskly boiled down to low bulk (5 cc.), till the oxides of iron and magnesium and most of the alumina have passed into solution. Add 5 cc. of HCl and 200 cc. of water, and bring the liquid to boiling, then little by little add down the lip of the covered

beaker dilute ammonia till a faint excess is present; boil for a few minutes. Collect (and preserve) the precipitated oxides of iron and aluminium on a 125 mm. pure filter. Wash them thoroughly with hot water, receiving the filtrate and washings into a clean 20-oz. beaker. The liquid is evaporated down to 20 cc., and when cold 20 cc. of strong ammonia solution are added, and then 10 cc. of 10 % solution of sodium phosphate. After standing some hours with an occasional brisk shaking round, the precipitated magnesia is determined in the manner described on p. 252.

Estimation of the FeO and Al_2O_3.—The well-washed precipitate of the mixed oxides of iron and aluminium is dried, ignited, and weighed in a platinum crucible in the usual manner. The residue is transferred without loss to a 10-oz. flask, and boiled with strong HCl till the whole of the iron and most of the alumina have dissolved. The liquid is then neutralized, reduced, and the percentage of iron is determined by titration exactly as described on p. 232 for iron ores. The result multiplied by 1·2857 = % FeO. The per cent. of Al_2O_3 is obtained by multiplying the weight of the double precipitate by 200, and from the product so obtained subtracting the percentage of metallic iron multiplied by 1·4286.

Example.

Weight of ore taken for analysis 0·5 gramme.

Weight of ($x\ Fe_2O_3 + y\ Al_2O_3$) = 0·1593 gramme.
cc. of $K_2Cr_2O_7$ required to oxidize iron 11·8

$$11{\cdot}8 \times 1{\cdot}2857 = \underline{\underline{15{\cdot}17}}\ \%\ FeO.$$

$$\begin{aligned}(15{\cdot}93 \times 2) &= 31{\cdot}86 \\ (11{\cdot}8 \times 1{\cdot}4286) &= \underline{16{\cdot}86} \\ &\quad \underline{\underline{15{\cdot}00}}\ \%\ Al_2O_3.\end{aligned}$$

Theoretical Considerations.

In the extract from the alkaline fusion the solution contains the silica and chromic oxide, together with a portion of the alumina respectively as alkaline silicate, chromate, and aluminate. The reaction by means of which the alumina is separated from the chromate with ammonium carbonate and CO_2 has been dealt with on p. 150. The insoluble residue contains the whole of the oxide of iron, the magnesia, and part of the alumina, the remainder of the latter being of course in the CO_2 precipitate. On dissolving up the two residues the three bases are obtained as chlorides free from chromium. The precipitate of oxide of iron and alumina carries down with it a little MgO, but the error so introduced is of small practical importance. In the same way small quantities of lime sometimes present are precipitated with the phosphate of magnesia. In cases where great accuracy is desired the iron and alumina may be precipitated twice, and the lime separated as oxalate by the process described for iron ores on p. 251.

Analysis of Wolfram.

This mineral consists essentially of ferrous tungstate, containing an appreciable percentage of MnO, and in smaller quantities, silica; occasionally about 1 % of lime is also present. It is seldom necessary to do more than estimate the WO_3, as the percentage of this constituent determines the value of the mineral for the production of ferro-tungsten.

Assay for WO_3.

(Time occupied, about $\frac{3}{4}$ day.)

Weight taken, and fusion.—Weigh out into a covered 3-in. platinum dish 0·6 gramme of the floured mineral, and fuse it over the gas blow-pipe for five minutes with a mixture of 3 grammes each of pure anhydrous sodic and potassic carbonates. *Potassic nitrate must not be employed.*

Extracting the fusion.—Place the dish and cover when cool in a 20-oz. beaker containing 200 cc. of nearly boiling water. When all soluble matter has been taken up the cover and dish are washed and removed.

Fractional filtration.—Transfer the liquid and residue without loss to a 300 cc. flask, make up to the mark, mix well, note the temperature, and filter off through a dry double paper 250 cc. corresponding to 0·5 gramme of ore.[1]

Precipitating the WO_3.—Transfer the solution without loss to a 20-oz. beaker, and neutralize the liquid with dilute nitric acid, free from nitrous acid. The acid is added little by little down the lip of the beaker till the last addition produces no further evolution of CO_2, showing the excess of alkaline carbonates to be completely decomposed and the nitric acid slightly in excess. The liquid must next be made neutral or *faintly* alkaline by the very cautious addition of a moderately strong solution of sodic carbonate. The exact point is carefully determined by placing on a white tile some small drops of a fairly strong aqueous solution of methyl orange indicator. As long as the liquid is acid the orange tint of the indicator is changed to a much richer, almost purple colour, when a

[1] At this stage alumina, if present, may be separated by the process described on p. 150.

small drop of the solution from the beaker is mixed with it, but the reaction is not affected by carbonic acid, so that when the free nitric acid has all been neutralized by the sodium carbonate, a drop of the liquid no longer changes the colour of the orange spots. The tungstic acid is next precipitated by bringing the solution almost to boiling, and adding, drop by drop, with constant and vigorous stirring with the glass rod, 3 cc. of a saturated solution of mercurous nitrate crystals in hot water. The tungsten is totally precipitated as mercurous tungstate Hg_2WO_4 mixed with basic mercurous nitrate: the rod is well washed, and the contents of the covered beaker are boiled for a few minutes, and are then allowed to digest on the corner of the plate till the precipitate has flocked out and the liquid is clear.

Filtering.—The somewhat bulky precipitate is collected on a 125 mm. pure paper contained in a 3-in. funnel. The precipitate is very thoroughly washed with nearly boiling water, but it must not be too vigorously disturbed, or some may pass through into the filtrate.

First ignition.—The precipitate is dried, ignited, and weighed when cold in a tared platinum dish. The ignition should at first be gentle, so as not to volatilize the mercury salts too violently, and so cause a mechanical loss of WO_3. The residue obtained is ($x\ WO_3 + y\ SiO_2$).

Removal of SiO_2 with HF and final ignition.—The residue is treated with about 2 cc. of pure aqueous hydrofluoric acid, and the latter is evaporated off in the draught cupboard. When the mass is dry the dish is again ignited, cooled, and weighed; the increase over the original weight of the dish is WO_3, containing 79·3 % of tungsten metal.

Example.

Weight of wolfram taken, 0·6 gramme.

$$\begin{aligned} \text{Weight of dish} + WO_3 &= 43{\cdot}6920 \\ \text{Weight of dish} &= 43{\cdot}3116 \\ \hline &\ {\cdot}3804 \text{ gramme } WO_3. \end{aligned}$$

$$\frac{\cdot 3804 \times 100}{0{\cdot}5} = 76{\cdot}08\ \%\ WO_3, \text{ or}$$

$$\frac{76{\cdot}08 \times 79{\cdot}3}{100} = 60{\cdot}33\ \%\ \text{Tungsten.}$$

Theoretical Considerations.

The fusion with alkaline carbonates converts the tungstic and silicic acids into soluble alkaline tungstates and silicates. The iron, magnesia, and lime remain insoluble as oxides and carbonates. The mercurous nitrate solution should be made just before required, by boiling several grammes of crystals of the pure salt with a few cc. of water. Any attempt to dilute the solution will cause a precipitation of basic nitrate. If the neutralization has been properly carried out, the trace of sodium carbonate in excess just serves to neutralize the free nitric acid in the mercurous nitrate solution, and the mercurous tungstate comes down in an almost perfectly neutral solution, a condition absolutely necessary for the complete precipitation of the tungstic acid. The presence of nitrites or nitrous acid renders the methyl orange insensitive, hence their absence must be carefully ensured.

SECTION III. REFRACTORY MATERIALS.

ANALYSIS OF GANISTER, SILICA BRICKS AND SANDS.

THE above materials consist almost entirely of silica, but contain in addition small percentages of alumina, ferric oxide, and lime. These impurities when present in small quantities, so far from being injurious, are valuable, from the fact that their presence causes the materials when used for furnace purposes to bind well without splintering or crumbling whilst being raised to the intense heat they are required to withstand. Of course, an excessive quantity of bases is fatal, causing the lining to fuse at steel-melting heat. Chemical analysis, however, does not completely decide the quality of ganister either in the raw state or in its manufactured form of silica bricks, inasmuch as materials practically identical in chemical composition may possess distinctly different physical properties.

Determination of Water and Organic Matter.

Weigh out about 2 grammes of the finely-divided material (previously passed through a sieve 90 meshes to the inch) into a tared platinum crucible, the cover of which is also weighed and left in the balance-case. The

material is strongly ignited in the muffle for about twenty minutes. The crucible after becoming quite cold in the desiccator is covered and re-weighed; the loss represents moisture and organic matter; the weight multiplied by 100 and divided by the weight of material taken = percentage.

Example.

Analysis of Deepcar silica brick.

Weight of crucible and cover = 34·4934
Weight of crucible, etc. + material = 36·5067

Weight of brick taken = 2·0133

Weight of crucible, etc., after ignition = 36·5030

36·5067 − 36·5030 = 0·0037 gramme = loss.

$$\frac{\cdot 0037 \times 100}{2\cdot 0133} = 0\cdot 18\ \%\ \text{loss on ignition.}$$

Determination of SiO_2, Al_2O_3, Fe_2O_3, and CaO.

(Time occupied, about 1½ days.)

Weight taken.—Weigh out into a deep 3-in. platinum dish 1 gramme of the finely-divided substance.

Fusing.—Intimately mix the material with 5 grammes each of sodic and potassic carbonates and half a gramme of KNO_3, and thoroughly fuse the contents in a covered dish over a gas blow-pipe for at least five minutes.

Extracting.—When cool, the dish and cover are placed in a 6-in. porcelain dish supported over a boiling water bath; the fusion is extracted with the smallest possible quantity of water, and the dish and cover are thoroughly washed and removed.

Double evaporation of HCl.—The porcelain dish is covered, and down the spout are poured 50 cc. of *HCl*,

previously heated in two portions in the covered platinum dish in which the fusion took place. When the evolution of CO_2 has ceased, the cover is rinsed and removed, and the contents of the dish are evaporated to complete dryness on the bath. When nearly dry, the mass is broken up with a glass rod, the dry powdery chlorides are then drenched with 25 cc. of HCl, are again evaporated to dryness, the dish being finally carefully heated over a Bunsen flame.

Estimating the SiO_2.—When cold, the perfectly dry mass is heated in the covered dish with about 20 cc. of HCl, and then with 100 cc. of water, till everything but the insoluble silica has passed into solution. The residue is collected on a 125 mm. pure paper, is washed first with hot dilute HCl and cold water alternately, and then very thoroughly with nearly boiling water.

The filtrate and washings are received into a clean 20-oz. beaker, and are preserved for the determination of the bases. The precipitate is dried, ignited, and weighed in a tared, covered crucible in the usual manner, and the weight multiplied by $100 = \%\ SiO_2$.

Separating the oxide of iron and alumina from the lime.—The filtrate from the SiO_2 is brought to boiling, and little by little dilute ammonia is added down the lip of the covered beaker till in faint excess; the liquid is boiled for a few minutes, removed from the plate, and the precipitate after settling somewhat is collected on a 90 mm. pure paper, thoroughly washed with hot water (the filtrate and washings being preserved in a clean 20-oz. beaker), dried, ignited, and weighed as $(x\,Fe_2O_3 + y\,Al_2O_3)$.

Estimating the Fe_2O_3.—The mixed precipitate is transferred without loss to a 10-oz. flask, the crucible being twice rinsed out with 10 cc. of boiling HCl, which is

poured into the flask and quietly boiled down to low bulk, till the whole of the Fe_2O_3 and most of the Al_2O_3 have dissolved. The acid liquid is then neutralized with very dilute ammonia, 1 in 10, reduced with 10 cc. of H_2SO_3 solution (be careful to boil off every trace of SO_2), and the iron is titrated in the usual manner[1] with a specially diluted standard solution of $K_2Cr_2O_7$, made by carefully measuring 100 cc. of the solution specified on p. 184 into a half-litre flask, diluting to the mark and well mixing. Each cc. required equals 0·1 % *Fe.* The number of cc. used multiplied by 0·14286 = % Fe_2O_3.

Calculating the Al_2O_3.—The percentage of Fe_2O_3 subtracted from the weight of the mixed precipitate multiplied by 100 = % Al_2O_3.

Estimating the lime.—The ammoniacal filtrate from the oxide of iron and the alumina is evaporated down to about 100 cc., made slightly alkaline with ammonia, and the lime is precipitated by boiling the solution after adding 10 cc. of a saturated solution of ammonium-oxalate. After digesting for some time the oxalate of calcium is allowed to settle, is collected on a 90 mm. pure paper, and is washed, dried, ignited, weighed, and estimated as oxide or sulphate in exact accordance with the instructions given on p. 252.

Examples of results obtained in the foregoing analysis.

Weight of SiO_2 obtained = 0·9617 gramme = 96·17 % SiO_2.

Weight of $(x\,Fe_2O_3 + y\,Al_2O_3)$ = 0·0209 gramme.

Cc. of $K_2Cr_2O_7$ used for iron = 7·5, and 7·5 × ·14286 = 1·07 % Fe_2O_3.

2·09 — 1·07 = 1·02 % Al_2O_3.

Weight of CaO = 0·0096 gramme = 0·96 % CaO.

[1] The addition of a few cc. of dilute H_2SO_4 must not be forgotten.

Precaution.

As sodic and potassic carbonates are seldom perfectly pure, it is very advisable to make a blank analysis on the same weight of mixed carbonates and nitre as that used for the fusion, and to estimate the SiO_2 and Al_2O_3 contained therein. The results are of course deducted from the respective constituents. If this precaution is neglected, the appreciable percentage of these substances sometimes present may cause the apparent percentage obtained to be distinctly high.

Theoretical Considerations.

On fusing, the ganister, etc. is decomposed by the alkaline carbonates into the silicates of soda and potash thus—

$$3\ SiO_2 + 4\ Na_2CO_3 = Na_8Si_3O_{10} + 4\ CO_2$$

Silica and sodium carbonate yield sodium trisilicate and carbon dioxide—

$$SiO_2 + K_2CO_3 = K_2SiO_3 + CO_2$$

Silica and potassium carbonate yield potassium metasilicate and carbon dioxide.

The alumina is converted partly into alkaline aluminate, partly into oxide, the lime and oxide of iron remain as such. On treating the extraction from the fusion with HCl the alkaline silicates are decomposed, forming chlorides and partially soluble silicic acid, the latter during the double evaporation to dryness is dehydrated and converted into insoluble SiO_2, whilst the lime, oxide of iron, and alumina form soluble chlorides. A single evaporation has not been found to render the whole of

the silica soluble, hence the mass is taken to dryness twice, and is finally ignited gently over the Bunsen flame. On taking up with *HCl* and water, the chlorides of aluminium, iron, calcium, and the alkalies pass into solution as chlorides. The lime is separated from the oxide of iron and alumina by taking advantage of the fact that its hydrate is not precipitated by ammonia. When great accuracy is desired, the oxide of iron and alumina may be precipitated twice, and the filtrate from the lime be examined for magnesia by the processes described for the analysis of iron ores.

Estimation of the Alkalies. (*See Fire-clays.*)

ANALYSIS OF FIRE-CLAYS AND BRICKS.

Fire-clays consist essentially of hydrated silicate of alumina containing greater or lesser percentages of the oxides of iron, calcium, magnesium, potassium, and sodium. The bases, particularly the two last named, if present in large quantities, are fatal to the refractory quality of the clay and bricks made therefrom. The steel chemist's horror, titanic acid, may also be present in small amount. The plastic properties of fire-clays depend upon the presence of a considerable percentage of combined water.

Determination of Hygroscopic Water.

The moisture present is estimated by the process given for iron ores on p. 230. The clay thus dried at 100° C. is finely pulverized, passed through a sieve of 90 meshes to the inch, and bottled for the remainder of the analysis, which will of course have reference to the dried material.

Determination of Combined Water and Organic Carbon.

The plastic water and organic carbon are most accurately determined by the method given for iron ores on p. 256. In clays free from FeO, however, their amount may be determined with sufficient exactness for practical purposes by igniting about 2 grammes of the clay. The details of the estimation are identical with those given for ganister on p. 275. When dealing with burnt fire-bricks, it is merely necessary to ignite the material and calculate and report the percentage of loss as total water and organic matter.

Determination of CaO and MgO.

Proceed on 1 gramme of the material as for ganister till the double precipitate of Al_2O_3 and Fe_2O_3 is obtained. This is collected on a 125 mm. paper, is allowed to drain, re-dissolved in HCl, the solution being received into the beaker in which the precipitation took place. The paper is washed and put aside till required for the second filtration. The yellow liquid is evaporated to low bulk, diluted to 200 cc., and re-precipitated with ammonia. The filtrate, which contains a small quantity of lime and magnesia, carried down by the alumina is added to the first filtrate containing the main quantity. The combined filtrates are evaporated to 200 cc., and the two constituents are then determined by the process described for iron ores on p. 252.

Determination of SiO_2 and Fe_2O_3.

SiO_2.—The SiO_2 in fire-clay, etc., is estimated on 1 gramme of the dry material by exactly the same process as that described for ganister: the final residue may contain a little TiO_2.

Fe_2O_3.—The filtrate from the silica is evaporated to low bulk, neutralized, reduced, and the percentage of iron is determined by titration as in the analysis of ganister.

The number of cc. of bichromate required multiplied by $0{\cdot}14286 = \%\ Fe_2O_3$.

Determination of Al_2O_3.

The alumina is very carefully determined working on 0·25 gramme of clay or brick (a larger weight gives a very unwieldy precipitate), by the process described for its estimation in ganister, but it should be twice precipitated to free it from lime and magnesia. The weight of the mixed precipitate multiplied by 400, minus the percentage of oxide of iron (as calculated from the titration made in the last article), equals % Al_2O_3.

A small percentage of TiO_2 may possibly be present in the double precipitate, and is registered as alumina.

Estimation of FeO.

The iron in fire-clays and bricks is usually reported as Fe_2O_3: it may, however, exist as *FeO*, in which form it is more injurious to the refractory qualities of the material owing to the comparative fusibility of ferrous silicate.

The proportion of ferrous oxide may be approximately estimated by the following process, due to Avery, Wilbur, and Whittlesey.

The Process.

One gramme of the material is reduced to impalpable powder in the agate mortar, and very intimately mixed with 1·5 grammes of finely-divided calcium fluoride (fluorspar), free from iron. The mixture is placed in a covered platinum dish, 20 cc. of strong HCl (devoid of free chlorine) are added. The mass is mixed with a platinum wire, and the dish is placed on the corner of the hot plate and digested for about an hour at a temperature slightly under 100° C. in an atmosphere of CO_2, in the apparatus sketched in Fig. 18, p. 241, for the determination of FeO in insoluble iron ores. The fire-clay crucible is merely placed over the dish on the iron plate. The solution is rinsed from the dish into a 20-oz. beaker containing 50 cc. of recently-boiled distilled water by means of a jet of the same liquid, and the ferrous iron is determined by titration, with the dilute standard bichromate solution specified for ganister on p. 277. The number of cc. required multiplied by 0·12857 = % FeO.

The percentage of Fe_2O_3 is obtained thus—

[cc. of $K_2Cr_2O_7$ required for total iron (in filtrate from SiO_2)] — (cc. required for FeO titration) × 0·14286 = % Fe_2O_3.

Determination of the Alkalies (Lawrence Smith, modified).

(Time occupied, about 2 days.)

Weight taken.—Weigh out 1·44 grammes of the substance *reduced to an impalpable powder* into a platinum dish, and intimately mix it with 1 gramme of pure ammonium chloride and 9 grammes of pure calcium carbonate (both re-agents must of course be quite free from potassium and sodium salts).

Dry fusion.—The covered dish is heated for about 1 hour in the muffle at a fair red heat, say 700° C.

Extracting the fusion.—When cold, the dry mass is detached and transferred without loss from the platinum to a 6-in. porcelain dish, heated on the water-bath with 250 cc. of water, the insoluble residue being broken up and afterwards occasionally pulverized with a small Wedgwood ware pestle during at least an hour.

Fractional filtration.—The pestle is rinsed, and the solution and residue are transferred without loss to a 302 cc. graduated flask, and when cold are diluted to the mark, thoroughly mixed, and 250 cc., corresponding to 1·2 grammes of material, are filtered off through a dry double filter into a graduated flask.

Removing the lime.—The 250 cc. of solution are transferred to an *old* 20-oz. beaker, boiled down to 200 cc., made alkaline with ammonia, and, a few cc. at a time, a saturated solution of pure ammonium oxalate is added till no further precipitation takes place. The beaker should be removed from the plate, and the oxalate allowed to settle between each addition, and about 5 cc. excess should be used. The liquid is boiled and afterwards quietly digested till the lime

has precipitated and the liquid is almost clear. The solution and precipitate are transferred to a 301 cc. flask, diluted to the mark, thoroughly mixed, and 250 cc. of liquid, corresponding to 1 gramme of material, are filtered off with the usual precautions.

Separating traces of MgO and CaO.—The 250 cc. of filtrate are boiled down and evaporated to about 40 cc., and made strongly alkaline with 10 cc. of 880 ammonia. Then add not more than three drops of a 10 % solution of ammonium phosphate, which must be quite free from potassium and sodium salts. The liquid is allowed to stand during some hours, being occasionally briskly shaken round. Any ammonium magnesium phosphate, together with a little oxalate of lime, which usually precipitates during the evaporation of the filtrate, is filtered off and washed with ammonia water, the filtrate and washings being received into an old clean 20-oz. beaker.

Removing P_2O_5.—The alkaline liquid is boiled down till almost free from ammonia, made faintly acid with HCl, and 5 cc. of the standard solution of $FeCl_3$ specified on p. 119 are added. The liquid is brought to boiling, and little by little dilute ammonia is poured down the lip of the covered beaker till in slight excess. The contents of the vessel are then quietly digested till the phosphate of iron has flocked out and the liquid is crystal clear. The precipitate is filtered off and washed with hot water, the filtrate and washings being received into a clean old 20-oz. beaker.

Removing ammonium salts.—Add to the filtrate from the phosphate of iron 30 cc. of strong nitric acid, and quietly boil the liquid down to 5 cc., then, with as little wash-water as possible, transfer the solution from the beaker to a tared 3-in. *porcelain* dish.

Weighing the alkalies as chlorides.—Quietly evaporate the liquid in the porcelain dish to very low bulk on a pipe-stem triangle placed on the hot plate; add 10 cc. of strong HCl and evaporate to dryness; cool the dish, add 5 cc. of HCl, again evaporate to dryness, and *gently* ignite over a Bunsen flame. When the dish has become quite cold in the desiccator, re-weigh it; the increase over the original weight of the dish = $(x\ KCl + y\ NaCl)$.

Estimating the chlorine.—Make a standard solution of nitrate of silver by dissolving 2·397 grammes of the pure dry salt in 50 cc. of water. Each cc. is equivalent to 1 milli-gramme of chlorine. (The solution may be standardized by means of a solution of pure dry $NaCl$, of which salt 0·0826 gramme dissolved in a little water should require exactly 50 cc. of the silver solution when titrated in the manner about to be described.)

The alkaline chlorides are dissolved by gentle boiling with 10 or 15 cc. of water, the dish is well rinsed out, the solution and washings being received in a 4-in. deep porcelain dish. Add to the liquid a few drops of a strong solution of yellow normal potassic chromate (K_2CrO_4),[1] and then from a 50 cc. burette slowly run in the silver solution, constantly stirring the liquid meanwhile till the last two drops of nitrate produce a permanent reddish tinge. Each cc. of standard solution used = 0·001 gramme Cl.

Calculating the alkaline oxides.—The percentage of the mixed oxides $(x\,K_2O + y\ Na_2O)$—and for practical purposes it is unnecessary to separate them—is calculated thus—(Weight of chlorides — weight of chlorine) + (weight of chlorine × 0·2256) = weight of $(x\ K_2O + y\ Na_2O)$, and

[1] This indicator is rendered more sensitive by adding a few drops of nitrate of silver solution, shaking well, and filtering off the clear solution from the precipitate of chromate of silver.

weight of mixed oxides multiplied by 100 = the percentage of alkaline oxides.

Example of Analysis.

Weight of clay taken 1·44 (= 1) grammes.	
Weight of dish + mixed chlorides =	43·6298
Weight of dish =	43·6112
Weight of ($x\ KCl + y\ NaCl$) =	·0186

Volume of silver solution required 9·8 cc. = 0·0098 gramme Cl.

Then (·0186 − ·0098) + (·0098 × ·2256) = ·0088 + ·0022 = 1·10 % of alkaline oxides.

Theoretical Considerations.

On heating, the $AmCl$ of the fusion mixture converts a portion of the $CaCO_3$ into chloride thus—

$$2\ AmCl + CaCO_3 = CaCl_2 + CO_2 + 2\ NH_3 + H_2O$$

The surplus carbonate of lime is converted into oxide with evolution of CO_2. The calcic chloride and oxide thus formed together attack the insoluble alkaline silicates, forming by a complex reaction silicate of lime and soluble potassic and sodic chlorides.[1] On extracting the fusion with water the calcium silicate, silica, alumina, and oxide of iron remain insoluble, whilst the alkaline chlorides, calcic chloride, together with some calcic oxide, and possibly a little magnesia, pass into solution. The bulk of the MgO, however, even if originally soluble, seems to be carried down with the carbonate of lime precipitated during the extraction owing to the action of atmospheric CO_2 on the calcic hydrate in solution. In the filtrate from the extraction the lime compounds are removed by precipitation as calcium oxalate, CaC_2O_4. The magnesia is precipitated as phosphate $AmMgPO_4$. The iron added is precipitated as

[1] The chlorides are volatile at about 800° C.

hydrate on the addition of ammonia, and carries down with it the excess of P_2O_5 as $FePO_4$. The removal of $AmCl$, etc. from the final solution by evaporating with HNO_3 has been explained on p. 254. The double evaporation with strong HCl is necessary to expel the nitric acid from the alkaline nitrates, and convert them into chlorides. The reaction between the chlorides and the silver nitrate may be exemplified thus—

$$KCl + AgNO_3 = AgCl + KNO_3$$

As soon as the whole of the chlorine has been reacted upon, the next addition of silver solution throws down from the yellow chromate of potash indicator a reddish precipitate of chromate of silver, thus—

$$K_2CrO_4 + 2\ AgNO_3 = Ag_2CrO_4 + 2\ KNO_3$$

In calculating the results, the factor given substitutes 1 atom of oxygen for the 2 atoms of chlorine, combined with the alkali metal, thus, diagramatically—

$$2\ KCl + 2\ NaCl + 2\ O = K_2O + Na_2O + 4\ Cl$$

$$\text{or} \quad K_1 \qquad Na_1 \qquad O_1 \quad \text{and} \qquad Cl_2$$

$$\begin{matrix} Cl_2 = 70{\cdot}74 \\ O_1 = 15{\cdot}96 \end{matrix} \quad \text{and} \quad \frac{15{\cdot}9}{70{\cdot}74} = 0{\cdot}2256 = \text{factor.}$$

It is very necessary that the analysis be conducted in old, well-used beakers; glass (which contains about 15 % of alkaline oxides) is palpably soluble when new, but the error from old beakers is small.

Analysis of Bauxite.

This mineral consists essentially of a double hydrate of aluminium and iron, containing about 50 % Al_2O_3, 25 % Fe_2O_3, 20 % H_2O, together with small percentages of silica, titanic acid, etc. It is sometimes used in the form of bricks as an isolating course in basic open-hearth furnaces.

Determination of Hygroscopic water.

The hygroscopic moisture is determined as for iron ores on p. 230. The remainder of the analysis is made on the mineral thus obtained dried at 100° C.

Estimation of Water of Constitution.

The combined water may be determined by simple ignition in the manner described on p. 274, when any little organic matter present will render the result obtained slightly high. It may be more accurately estimated by the process described for iron ores on p. 256.

Determination of SiO_2.

One gramme of the finely-divided mineral is fused with 3 grammes each of pure sodic and potassic carbonates, the fusion is extracted in porcelain, and evaporated twice to dryness on the water-bath with strong HCl. The dry mass is taken up in HCl and water, the insoluble silica being filtered off, thoroughly washed, dried, ignited, and weighed in the usual manner. It will probably contain a little TiO_2.[1] The details of the above operations will be sufficiently obvious on reference to the articles on the analysis of ganister and fire-clay.

Preserving the filtrate.—The filtrate and washings from the SiO_2 are received into a 250 cc. graduated flask; the liquid is cooled, made up to the mark, well mixed, and

[1] The SiO_2 may, if desired, be purified by fusion with $HKSO_4$ (see p. 194).

portions are employed for the estimation of the Al_2O_3 and Fe_2O_3.

Determination of Ferric Oxide.

Measure off 125 cc. of the filtrate from the silica, corresponding to 0·5 gramme of bauxite, into a 20-oz. flask. The liquid is then neutralized, reduced, acidified, titrated, and the percentage of Fe_2O_3 calculated as though dealing with an iron ore.

Estimation of Alumina.

50 cc. of the filtrate from the silica, corresponding to 0·2 gramme of bauxite, are measured into a 20-oz. beaker, diluted to 200 cc., brought to boiling, and the oxide of iron and alumina are precipitated by pouring down the lip of the covered beaker a faint excess of dilute ammonia. The precipitate after digesting is filtered off on a 125 mm. pure paper, slightly washed, re-dissolved in HCl, re-precipitated with ammonia, and is filtered off, thoroughly washed with hot water, dried, ignited, and weighed as $(x\,Al_2O_3 + y\,Fe_2O_3)$. The percentage of Al_2O_3 is calculated by difference in the manner described on p. 277, of course using the percentage of Fe_2O_3 as determined in the last article. The result will probably be a little high, small quantities of $K_2O_5TiO_2$ being estimated as alumina.

ANALYSIS OF MAGNESIAN LIME BRICKS.

The operation of crushing these bricks must be performed as expeditiously as possible, so as to quickly get the pulverized material into a closely-stoppered bottle, as it is very liable to absorb moisture and CO_2 from the air.

Estimation of SiO_2.

Dissolve 1 gramme of the pulverized brick in 20 cc. of HCl, evaporate to dryness, take up in HCl, filter off the insoluble SiO_2, thoroughly wash with HCl and water, and dry, ignite, and weigh in the usual manner. The weight obtained multiplied by $100 = \%\ SiO_2$. The residue may contain small quantities of basic oxides, and where scientific accuracy is required, a considerable quantity of it may be analyzed as if a sample of ganister, the magnesia being of course determined.

Determination of Alumina and Oxide of Iron.

Dissolve 2 grammes of the powdered brick in 30 cc. of HCl, dilute the solution to 200 cc., bring to boiling, and precipitate the oxide of iron and alumina with a faint excess of ammonia. Filter off the precipitate, wash it slightly, re-dissolve in HCl, and re-precipitate as before. Thoroughly wash the precipitated oxides with boiling water, dry, ignite and weigh as $(x\ Fe_2O_3 + y\ Al_2O_3)$. The residue, however, may contain traces of Mn_3O_4 and P_2O_5. It is boiled with HCl, and when all the iron has passed into solution the liquid is neutralized, reduced, and the iron is titrated in the usual manner, with the bichromate solution specified on p. 277 for ganister. The result obtained is, however, divided by two, the respective percentages of oxide of iron and alumina are then calculated as usual.

Determination of Lime and Magnesia.

0·5 gramme of material is dissolved in HCl and evaporated to dryness; the mass is taken up in 5 cc. of HCl, diluted to 200 cc., and the oxide of iron and alumina are precipitated with dilute ammonia. They are filtered off and slightly washed, the filtrate and washings being preserved. The precipitate from the ammonia is redissolved in HCl, the solutions and washing being received into the beaker in which the precipitation took place. The liquid is evaporated to 5 cc., and diluted, precipitated with a faint excess of ammonia as before. The precipitate is filtered off, and the resulting filtrate, probably containing a little lime and magnesia, is added to that containing the main quantities. The solution is evaporated to 200 cc., and the lime is precipitated with 20 cc. of a saturated solution of ammonium oxalate, and estimated in the manner described for iron ores on p. 252.

MgO.—The filtrate from the calcium oxalate is acidified with HCl, evaporated down to about 100 cc., and 25 cc. of a 10 % solution of ammonium phosphate are added, then, constantly shaking the liquid round, add dilute ammonia till in distinct excess. The total volume is then made up with strong ammonia to 200 cc. After standing a few hours with an occasional brisk shaking, the phosphate is filtered off, washed with water strongly alkaline with ammonia, and is dried, ignited, and weighed as $Mg_2P_2O_7$ in the usual manner, 4 milligrammes being added to the weight of the precipitate as a correction for solubility. The corrected weight of pyrophosphate multiplied by 72·2 = % MgO.

Analysis of Dolomite.

Typical dolomite consists of a double carbonate of lime and magnesia containing about 48 % CO_2, 30 % MgO, 20 % CaO, and as impurities, small percentages of FeO, MnO, Al_2O_3, and SiO_2. Small quantities of SO_3, FeS_2, P_2O_5, and TiO_2 may also be present in this mineral, and consequently the compounds resulting from their ignition may be found in the magnesian lime bricks made from it. An exhaustive analysis, however, is seldom necessary for practical steel works purposes. The analytical procedure given below is of course applicable to ordinary limestone ($CaCO_3$+impurities) and magnesite ($MgCO_3$+impurities).

The methods for estimating in limestones SiO_2, FeO, Al_2O_3, CaO,[1] MgO,[2] do not differ in their details from those given in the previous article.

CO_2.—Carbon dioxide is estimated by the process described for carbonated iron ores on p. 255.

Determination of MnO.

Dissolve 12 grammes of the pulverized stone in dilute HCl in a large covered beaker, and evaporate to low bulk. Transfer the solution and insoluble residue to a 600 cc. graduated flask; when cold, make up to the mark, thoroughly mix, and by fractional filtration obtain 500 cc. of liquid containing the MnO in 10 grammes of dolomite. Transfer the liquid to a 30-oz. registered flask, add 4 cc. of bromine, shake the liquid till it is nearly all dissolved, and then add cautiously 50 cc. of strong ammonia. The

[1] Weight of $CaO \times 1{\cdot}7846 = CaCO_3$.

[2] Per cent. $MgO \times 2{\cdot}125 = \%\ MgCO_3$.

solution is shaken round and then digested, nearly at boiling, till clear. The precipitate is filtered off, washed, dissolved in HCl, the solution and washings being neutralized with ammonia and the iron precipitated with ammonium acetate. The ferric acetate is filtered off; the manganese in the filtrate is precipitated with bromine and ammonia, and estimated in the usual manner. The weight of Mn_3O_4 obtained $\times 0{\cdot}93 =$ the weight of MnO: this $\times 10 = \%$ MnO.

Estimation of P_2O_5 and Sulphur.

P_2O_5.—Dissolve 10 grammes of the pulverized mineral in a 20-oz. covered beaker in 50 cc. of HCl. Evaporate to low bulk, and dilute to 200 cc. Bring the liquid to boiling, and precipitate the Fe_2O_3, Al_2O_3, and P_2O_5 with a faint excess of ammonia. Filter off the precipitate, wash it, and re-dissolve in HCl; evaporate the solution and washings to low bulk, add excess of dilute ammonia, just take up the resulting precipitate in strong nitric acid, boil for a few minutes, remove the beaker from the plate, and add excess of nitric acid solution of ammonium molybdate specified on p. 123. The resulting yellow precipitate is filtered off and weighed in accordance with the directions given for the estimation of phosphorus in steel. The weight obtained, multiplied by $3{\cdot}73$ and $\div 10 = \%$ P_2O_5.

S.—Sulphur is estimated working on 6 grammes of the stone as in the case of an iron ore; the remarks made on p. 248 concerning the insoluble residue apply also to the present case.

Determination of Alkaline Oxides.

The alkalies in raw dolomite or in its burnt form as bricks may be determined by fusing respectively 10 or 5 grammes of the material in impalpable powder with 1 gramme of ammonium chloride and proceeding by the process described for fire-clay on p. 283, the result being of course calculated on 10 or 5 grammes as the case may be.

SECTION IV. FUELS.

COAL.

Coal is a fossil fuel resulting from the accumulation of vegetable matter during past geological ages. The duration of the action of mechanical pressure of superimposed strata and internal chemical change, determine the character of the coal, which ranges from incompact, peaty brown coal, through the ordinary black pit coal to compact, vitreous anthracite, the last-named being the oldest formation. Chemically, coal consists mainly of carbon, together with varying quantities of hydrogen, oxygen, a little nitrogen, and the inorganic constituents found in its ash. The most noticeable chemical change marking the inconceivably slow passage from peat to anthracite is a diminution of oxygen, accompanied by a consequent increase of carbon and heating power.

Proximate Analysis of Coal.

The industrial analysis of coal usually includes the following items—

Moisture.

Coke (= fixed carbon + ash).

Volatile matter (= weight of original dry coal — coke).

Sulphur.

Ash.

Determination of Moisture.

The process described for iron ores on p. 230 may also be employed for coal, using 2 grammes of the powdered mineral, and heating it for about an hour in the air-bath at a temperature slightly over 100° C.

Determination of Coke.

(Time occupied, about 4 hours.)

Take a covered clay crucible $2\frac{1}{4}$ in. diameter and $2\frac{1}{2}$ in. deep (inside dimensions), and on a stone slab grind the cover and top of the crucible truly flat, so that the former fits closely all round the latter. Weigh out into the crucible 25 grammes of the coal in powder, put on the cover, and without disturbing it place the crucible in the muffle furnace, inserting the lower door. The heat is continued till the gas flame, emerging from between the crucible and cover, has practically ceased to burn; the whole is then carefully removed without displacing the cover, and allowed to cool on an iron plate. When cold, the lid is removed, the coke is detached and weighed without loss, and the weight multiplied by 4 = % coke. The nature of the latter should also be noted; good caking coal leaves the coke in a hard, compact mass, forming a cast of the inside of the crucible owing to the tar formed at the commencement of the heating, causing the coal to assume a state of semi-fusion. On the other hand, anthracitic coal only forms a fritted mass of incoherent granules, owing to the absence of the binding of carbonized tar.

Estimation of Sulphur (Eschka, modified).

(Time occupied, about ¾ day.)

Weight taken.—Weigh out 1·2 grammes of the coal in a very fine state of division into a 2½-in. flat platinum dish, and very intimately mix it with about 1·25 grammes of calcined magnesia and 0·6 gramme of anhydrous sodium carbonate. The mixture is tapped down and covered with a layer of about half a gramme of magnesia.

Blank estimation.—A blank determination of the sulphur in the weight of re-agents used must be made, and the $BaSO_4$ obtained is deducted from that resulting from the analysis of the coal.

Dry fusion.—Place the uncovered dish in the muffle at a moderate red heat for about an hour till the coal has burned off and no black particles of coke remain.

Extracting.—When cold, the dish is placed in a 20-oz. beaker containing 80 cc. of boiling water. When the mass has disintegrated the dish is rinsed with hot water and removed. The contents of the covered beaker are digested at incipient boiling for about half-an-hour.

Fractional filtration.—The solution and residue are carefully transferred without loss to a 120 cc. graduated flask, and when cold are made up very slightly over the mark, thoroughly mixed, and 100 cc. of clear solution, containing the sulphur in 1 gramme of coal, are filtered off through a dry double filter.

Precipitating the sulphur.—The 100 cc. of liquid are washed out into a 20-oz. covered beaker, and 10 cc. of bromine water and afterwards about 5 cc. of HCl are added. The liquid is brought to boiling, and 10 cc. of 10 % solution of $BaCl_2$ are poured down the lip of the beaker. The boiling

is continued for about 15 minutes, when the $BaSO_4$ should be granular, and not so liable to pass through the filter-paper as when precipitated cold. It is allowed to settle somewhat, is collected on a 90 mm. pure paper, washed, dried, ignited, and weighed with the precautions given on p. 98 *et seq.* The corrected weight obtained multiplied by $13 \cdot 7 = \% \ S$.

Theoretical Considerations.

The sulphur in coal is known to exist in at least two forms, namely, as SO_3 in the metallic sulphates constituting several units per cent. of the inorganic ash, and in brassy scales and particles of iron pyrites FeS_2.

In the foregoing analysis, both forms of sulphur are converted mainly into the soluble sulphates of magnesium and sodium; small quantities of the sulphides of those metals may also be formed. The latter are converted into sulphates by the oxidizing action of the bromine water added to the extract from the fusion.

Determination of Ash.

2 grammes of the powdered coal are placed in a tared platinum crucible, the weighed cover being left in the balance-case. The organic constituents of the coal are burnt off in the muffle very cautiously at first, till the ash is free from dark specks of coke. Its colour may be nearly white, red, or grey. The crucible is allowed to go quite cold in the desiccator, and is then covered and re-weighed: the increase in weight multiplied by 100 and $\div 2 = \%$ ash.

Precaution.—The initial heating of the coal must be very gentle till the mineral has coked, otherwise the violent evolution of gas may carry away some of the ash.

Analysis of Coal Ash.

When an analysis of the ash of coal is required several grammes must be prepared and weighed out as required, from a well-stoppered bottle. The various constituents will be seen on reference to the analysis given on p. 342. The silica, oxide of iron, alumina, magnesia, and alkalies are determined as if the substance under examination were a fire-clay. The SO_3 is determined on half a gramme of ash by the process specified on p. 248 for the analysis of the insoluble residue from iron ores.

Determination of P_2O_5.

One gramme of the ash is fused with 3 grammes each of a mixture of sodic and potassic carbonates free from phosphorus: the fusion is extracted in HCl, the solution made slightly alkaline with dilute ammonia, and the oxide of iron and alumina are filtered off and slightly washed. The precipitate, which contains the whole of the P_2O_5, is re-dissolved in HCl, the solution and washings are evaporated to low bulk, and the phosphoric acid is determined by the combined process described for the estimation of phosphorus in steel on p. 125. The corrected weight of $Mg_2P_2O_7$ $\times 63{\cdot}96 = \%\ P_2O_5$.

Elementary Analysis of Coal.

The determination of the percentage of carbon and hydrogen in coal is seldom required in steel works practice. The analysis is made by the process described for the determination of combined water and organic carbon in iron ores on p. 256. Exactly 0·2 gramme of the coal is weighed out into a porcelain boat for the analysis. The increase of weight in the sulphuric acid bulb multiplied by 55·65 = % *H*. The increase in the potash and chloride of calcium tubes × 136·35 = % *C* when precisely 0·2 gramme of coal is burnt: water containing 11·13 % *H* and CO_2, 27·27 % *C*.

Analysis of Coke and Charcoal.

The processes just described for coal are also applicable to coke and charcoal.[1]

Analysis of Producer Gases.

Gaseous fuel as employed for open-hearth furnaces seldom contains more than 40 % by volume of combustible gases, the remainder being chiefly nitrogen, together with a few units per cent. of CO_2 and possibly traces of oxygen. The gases useful for fuel are hydrogen, carbonic oxide CO, and marsh gas or light carburetted hydrogen CH_4. A small amount of olefiant gas or heavy carburetted hydrogen C_2H_4 may also be present. The determination of oxygen and

[1] In estimating the moisture in charcoal the latter may require a prolonged heating at a temperature considerably over 100°. It should then be weighed quickly, as it is capable in a damp atmosphere of absorbing a considerable weight of moisture, etc.

C_2H_4 is hardly necessary for practical purposes: the amount of the former is so minute and the separate determination of the inconsiderable percentage of the latter usually present so complicates the analysis as to render it inadvisable. Its elements, moreover, will be reported as CH_4 and CO, so making an inappreciable difference in any calculation of the calorific intensity of the gas made on the result of the analysis.

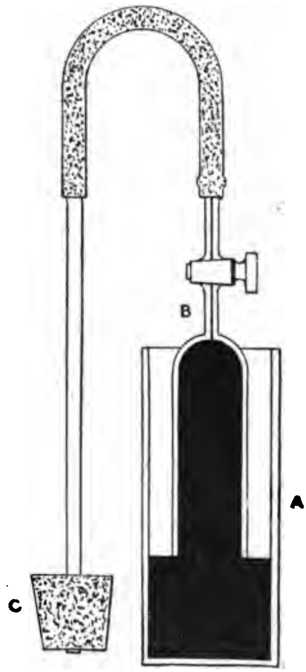


FIG. 19.

The Process.

(Time occupied, about 1 hour.)

Sampling.—This operation is carried out in the simple apparatus sketched in Fig. 19. A is a glass cylinder 5 in. long by 2 in. diameter. It is about one-third filled with mercury. In it is placed the laboratory vessel B, also (by suction) filled with mercury right up to the end of the capillary tube above the tap, the latter being then closed. C is a cork slightly carbonized outside, fitting the sampling aperture in the gas main and carrying a glass tube and piece of thick-walled india-rubber tubing. The cork is inserted in the sampling hole, and in close producers a flush of gas is put on by widely opening the steam jets.

When the gas is freely issuing from the end of the india-rubber tubing the latter is slipped over the capillary tube of the laboratory vessel; the tap is opened, the gas drawn in till the vessel is about half full, when the tap is closed, and the india-rubber tubing detached.

Analyzing the Gas.

The volumetric analysis of the gas is conveniently made in the apparatus designed for this purpose by Mr. J. E. Stead, which is essentially that sketched in Fig. 20. It is placed in a large square tray to prevent the loss of mercury accidentally spilled.

Measuring off a definite volume.—Over the capillary tube of the laboratory vessel containing the gas is slipped a piece of thick-walled india-rubber tubing, which is then filled with mercury.

The laboratory vessel and its capillary attachments up to B are filled with *KHO* solution (1 in 3), drawn up from the cylinder by previously filling the eudiometer tube with mercury, and then lowering the reservoir M. The tap B is then quickly closed.

The tap A is opened; the reservoir of mercury M is raised by pulling down the weight W till mercury drips from the end of the capillary tube at C. The tap is then closed. The india-rubber tubing of the gas vessel having been firmly slipped over C, the reservoir M is lowered, the tap A and that of the gas vessel are opened, and about 80 volumes of gas are drawn into the graduated eudiometer tube E. Both taps are then closed and the gas vessel detached. The reservior M is next carefully adjusted till the levels of the mercury menisca in the tubes E and P are exactly coincident when sighted

across the top of the adjusting level L. Carefully note the number of volumes of gas in the eudiometer (first reading).

First absorption.—Raise the reservoir M and open the tap B till the gas has passed into V, and mercury drips into the vessel; then close the tap. Whilst the potash is absorbing the CO_2 open the tap A, till mercury drips from C, thus sweeping out the gas in the capillary between E and A; then close A. In five minutes M is lowered, the tap B opened, and the gas is transferred back to E, *taking great care not to let the KHO solution get past* B. The levels having been carefully adjusted, the reading is again noted (second reading).

First explosion.—Introduce from a glass gas-holder containing pure oxygen (prepared from $KClO_3$ and well washed through caustic soda) about 30 volumes of the gas, being very careful to allow the oxygen to sweep out all the air in the india-rubber tubing from the gas-holder before attaching it to C. A is closed, the columns are levelled, and the volume noted (third reading). From the terminals of a sufficiently powerful Ruhmkorff coil worked by two bichromate cells, pass a spark through the platinum wires fused in at the top of the tube E.[1] After the explosion temporarily set the levels, wait till the heat produced has radiated, and the reading is constant (fourth reading).

Second absorption.—Pass the gas as before into V for five minutes, return to E, level and read off (fifth reading).

[1] If the spark will not pass some *KHO* solution has probably passed into the tube, and the current is passing round the glass instead of across the spark terminals. In such a case return the gas into V and wash out E with dilute *HCl*, and then two or three times with distilled water. Return the gas to E when the spark will pass.

Second explosion.—Next introduce from a gas-holder, with the same precaution as in the case of oxygen, about 50 volumes of pure hydrogen (prepared from HCl and redistilled zinc free from carbon); level and read off (sixth reading). Again explode, cool, and note the volume (seventh reading).

Calculating the volumes.—

Let difference between	1st and 2nd	reading	$=a=$	Contraction after 1st absorption.
,, ,, ,,	2nd and 3rd	,,	$=b=$	Volume of added oxygen.
,, ,, ,,	3rd and 4th	,,	$=c=$	Contraction after 1st explosion.
,, ,, ,,	4th and 5th	,,	$=d=$	Contraction after 2nd absorption.
Let the	5th	,,	$=e=$	Volume after 2nd absorption.
Let difference between	6th and 7th	,,	$=f=$	Contraction after 2nd explosion.

Then—

$$\text{Volume of } CO_2 = a$$
$$\text{,, ,, } CO = \tfrac{1}{3}(4d + c + f) - b$$
$$\text{,, ,, } H = c + \tfrac{1}{3}f - b$$
$$\text{,, ,, } CH_4 = b - \tfrac{1}{3}(d + c + f)$$
$$\text{,, ,, } N = e - \tfrac{1}{3}f$$

Example.

Analysis of gas entering the open-hearth furnace, Sheffield Technical School. Producer not working satisfactorily.

1st	Reading	87·5	vols.			
2nd	,,	81·0	,,	diff. 6·5	vols.	$= a$
3rd	,,	127·0	,,	,, 46·0	,,	$= b$
4th	,,	95·0	,,	,, 32·0	,,	$= c$
5th	,,	73·0		,, 22·0	,,	$= d$
6th	,,	150·5	,,	73·0	,,	$= e$
7th	,,	80·0	,,	diff. 70·5	,,	$= f$

Then :—

$$CO_2 = \qquad 6{\cdot}5 \text{ vols.}$$
$$CO = \frac{88{\cdot}0 + 32{\cdot}0 + 70{\cdot}5}{3} - 46 = 63{\cdot}5 - 46 = 17{\cdot}5 \text{ ,,}$$
$$H = 32 + 23{\cdot}5 - 46 = 55{\cdot}5 - 46 = 9{\cdot}5 \text{ ,,}$$
$$CH_4 = 46 - \frac{22 + 32 + 70{\cdot}5}{3} = 46 - 41{\cdot}5 = 4{\cdot}5 \text{ ,,}$$
$$N = 73 - \frac{70{\cdot}5}{3} = 73 - 23{\cdot}5 = 49{\cdot}5 \text{ ,,}$$
$$\overline{87{\cdot}5}$$

Then to convert volume into percentage.

$$\frac{6 \cdot 5 \times 100}{87 \cdot 5} = 7 \cdot 4\ \% \text{ by vol. of } CO_2$$

$$\frac{17 \cdot 5 \times 100}{87 \cdot 5} = 20 \cdot 0 \quad ,, \quad ,, \quad CO$$

$$\frac{9 \cdot 5 \times 100}{87 \cdot 5} = 10 \cdot 9 \quad ,, \quad ,, \quad H$$

$$\frac{4 \cdot 5 \times 100}{87 \cdot 5} = 5 \cdot 1 \quad ,, \quad ,, \quad CH_4$$

$$\frac{49 \cdot 5 \times 100}{87 \cdot 5} = 56 \cdot 6 \quad ,, \quad ,, \quad N$$

Theoretical Considerations.

The reactions involved in the above operations are as follows :—

The CO_2 present is absorbed in the caustic potash with formation of K_2CO_3.

On exploding the remaining gas with excess of oxygen the nitrogen remains unaltered, but the hydrogen, carbonic oxide, and marsh gas are converted into gaseous carbon dioxide and liquid water, thus :—

$$\underset{\text{2 vols.}}{2\,H} + \underset{\text{1 vol.}}{O} = \underset{\text{0 vol. (practically)}}{H_2O}$$

$$\underset{\text{2 vols.}}{CO} + \underset{\text{1 vol.}}{O} = \underset{\text{2 vols.}}{CO_2}$$

$$\underset{\text{2 vols.}}{CH_4} + \underset{\text{4 vols.}}{4\,O} = \underset{\text{2 vols.}}{CO_2} + \underset{\text{0 vol.}}{2\,H_2O}$$

The total CO_2 formed is absorbed by the second treatment with KHO.

In the second explosion the surplus oxygen is converted into water, leaving the nitrogen and some surplus hydrogen. The contraction after the first explosion = (the volume of hydrogen + $\frac{1}{2}$ its volume of oxygen) + (oxygen equivalent to $\frac{1}{2}$ the volume of CO) + (oxygen equivalent to twice the volume of CH_4). The contraction after the second ab-

sorption = (volume of CO) + (volume of CH_4). The contraction after the second explosion = (volume of surplus oxygen) + (twice its volume of hydrogen).

The various volumes measured do not require correcting for variations in temperature, pressure, or humidity, because during an analysis the thermometer and barometer do not sensibly alter, and the gas as it comes from the producer and throughout the analysis may be regarded as having a constant tension, viz. that due to uniform saturation with aqueous vapour.

(If it is desired to use the volumetric analysis of the gas for calculating its theoretical calorific intensity, proceed in accordance with the instructions and examples given in the Appendix on p. 335.)

Rapid analytical Valuation of Producer Gas.

If rapidly obtained results sufficiently near the truth to form a guide for practical working are desired, the estimation of the CH_4 may be omitted, its elements reported as CO and H, and the nitrogen by difference.

In this case the process is considerably simplified, becoming as follows :—

(1) Measure off a definite bulk (80 vols.) of the gas = 1st reading
(2) About the CO_2 in the potash. Vol. afterwards = 2nd ,,
(3) Add about 30 vols of oxygen. Vol. afterwards = 3rd ,,
(4) Explode the gases. Vol. afterwards (when cold) = 4th ,,
(5) Absorb the CO_2 formed in potash. Vol. afterwards = 5th ,,

Let (a) = Difference between 1st and 2nd reading.
,, (b) = Difference between 3rd and 4th reading.
,, (c) = Difference between 4th and 5th reading.

Then—

$$CO_2 = a$$
$$CO = c$$
$$H = \tfrac{2}{3}\,(b - \tfrac{1}{2}\,c)$$

Precautions.—The taps of the gas apparatus should be slightly smeared with vaseline, and great care should be taken not to let those coming into contact with the caustic potash set in the sockets; otherwise the apparatus may be broken in attempts to loosen them. When not in frequent use the taps should be removed, and be replaced for the time being by corks to keep dust out of the capillaries.

SECTION V. SUNDRIES.

ANALYSIS OF SLAGS.

In order to avoid unnecessary repetition of analytical details already fully described in connection with iron ores and refractory materials, the author purposes with reference to slags to give only brief, skeleton instructions for their analysis. Cinders of five typical constitutions will be dealt with, which may be divided into two classes—

1. Slags insoluble in HCl, and which therefore require fusion with alkaline carbonates to render their bases soluble.

2. Slags practically soluble in strong HCl.

The first class includes—

(*a*) Blast furnace slags, which consist of a neutral double silicate of lime and alumina.

(*b*) Finery slag, consisting essentially of ferrous silicate.

(*c*) Slag from the acid Bessemer process, consisting of a double silicate of the protoxides of manganese and iron.

The second class comprises—

(*a*) Slag from the basic process, consisting chiefly of basic phosphate of lime.

(*b*) Tap cinder from the puddling furnace, consisting mainly of a highly basic silicate of ferrous and ferric oxides.

Analysis of Blast Furnace Slag.

SiO_2.—Fuse 0·5 gramme of the finely-divided slag with a mixture of 2 grammes each of Na_2CO_3 and K_2CO_3, and 0·5 gramme of KNO_3 in a platinum dish. Extract in a porcelain dish with water, evaporate twice to dryness with HCl on the water-bath, take up in HCl and water, filter off, and estimate the SiO_2, preserving the filtrate and washings.

Al_2O_3 and Fe_2O_3.—The oxide of iron and alumina are precipitated in the filtrate from the SiO_2 in a bulk of 200 cc. with a faint excess of ammonia. The precipitate is filtered off (the filtrate being preserved), re-dissolved in HCl, and re-precipitated with ammonia. The precipitate is collected, washed, dried, ignited, and weighed as $(x\ Al_2O_3 + y\ Fe_2O_3)$, the second filtrate being added to that from the first precipitation.

CaO and MgO.—The double filtrate is evaporated down, and in it the lime and magnesia are estimated as in an iron ore containing a considerable percentage of manganese.

FeO.—Fuse 3 grammes of the slag with 12 grammes each of K_2CO_3 and Na_2CO_3. The fusion is extracted with HCl, the solution evaporated down till the oxides of iron and manganese have totally dissolved, and is then boiled with the addition of 1 cc. of strong HNO_3. The liquid having been made up to a definite volume, $\frac{5}{6}$ths, corresponding to 2·5 grammes of slag, are filtered off. The solution is neutralized with ammonia, the iron precipitated with ammonium acetate, filtered off (the filtrate and washing being preserved), re-dissolved in HCl, neutralized, reduced, and titrated with the standard bichromate solution employed for iron ores. The number of cc. required $\div\ 5 =$ $\%\ Fe$; this $\times\ 1·2857 = \%\ FeO$.

Al_2O_3.—The number of cc. above required × 1·4286 = % Fe_2O_3, which deducted from the combined percentage of ($x\ Fe_2O_3 + y\ Al_2O_3$) = % Al_2O_3.

MnO.—The filtrate from the acetate of iron is cooled, saturated with bromine, and the manganese mixed with some alumina is precipitated with excess of ammonia. The precipitate is filtered off, dissolved in *HCl*, evaporated to low bulk, boiled with excess of strong nitric acid, and the manganese is estimated by the Ford and Williams process described on p. 84, having previously added 2·5 grammes of Swedish iron in nitric acid solution. The manganese in the iron must be deducted from the result obtained. The corrected percentage of manganese × 1·2909 = % *MnO*.[1]

Sulphur.—The sulphur (probably existing as calcium sulphide) is determined by the process given for the insoluble residue from iron ores on p. 259. It may also be tried by the volumetric lead acetate process, which will register the amount actually existing as calcium sulphide, the difference between which and the total amount obtained by fusion gives the sulphur existing as SO_3.

P_2O_5.—The phosphoric acid may be determined by the method given for estimating the phosphorus in the insoluble residue from titanic pig-iron on p. 198.

Alkalies.—The alkalies are determined as in a fire-clay.

[1] If the standard bichromate solution and weight of iron specified for estimating the manganese in steel are employed, the percentage of manganese obtained must be doubled, inasmuch as only that in 2½ grammes of slag is present.

Analysis of Finery Slag.

SiO_2.—Fuse 0·5 gramme of the finely-divided slag as in the case of the blast-furnace product. The fusion is extracted in water, and evaporated twice to dryness on the water-bath. The bases having been taken up in *HCl* and water, the residual silica is filtered off and determined as usual.

FeO.—In the acid filtrate (and washings) from the silica the iron is precipitated with ammonia, filtered off, re-dissolved in *HCl*, neutralized, reduced, and titrated as in the case of an iron ore. The number of cc.s required × 1·2857 = % *FeO.*

MnO, P_2O_5, S.—The manganous oxide, phosphoric acid, and sulphur are estimated in the manner described for the analysis of blast-furnace slag.

CaO, MgO.—1·2 grammes of the slag are fused with 10 grammes of fusion mixture, extracted, evaporated, and the silica is separated by filtration in the manner described for *SiO_2*. From the filtrate the oxide of iron and alumina are twice precipitated with ammonia, and in the evaporated double filtrate the lime and magnesia are determined as usual, the manganese being separated as sulphide in the manner described on p. 251, and the *CaO* and *MgO* results being calculated to percentage on 1 gramme.

Al_2O_3.—The precipitate of oxide of iron and alumina from the last filtration is re-dissolved in *HCl*, neutralized, reduced, and the alumina determined as phosphate as in the case of an iron ore, the result being of course calculated on 1 gramme.

Acid Bessemer Slag.

SiO_2.—Fuse 0·5 gramme of the finely-divided slag with 3 grammes each of K_2CO_3 and Na_2CO_3. The fusion is extracted in HCl, the silica is rendered insoluble by evaporation to dryness, and is determined as usual.

MnO.—The filtrate (and washings) from the SiO_2 is saturated with bromine, and the manganese precipitated with excess of ammonia. The precipitate is filtered off, re-dissolved in HCl, the filtrate and washings being received into a 20-oz. covered beaker, to which is then added 0·5 gramme of pure Swedish bar-iron. When, on boiling, the latter has dissolved, the solution is oxidized with a few drops of strong HNO_3, evaporated to low bulk, and the manganese is determined by Pattinson's method as on p. 202. From the manganese registered is deducted the small amount present in the Swedish iron, and the remainder multiplied by 1·2909 = % MnO.

CaO, MgO.—Fuse 2·4 grammes of the finely-pulverized slag with 9 grammes of K_2CO_3, 9 grammes Na_2CO_3, and 2 grammes of KNO_3, the whole being intimately mixed. The fusion is extracted in water, evaporated to dryness with HCl, the silica separated by filtration, and the filtrate and washings when cold are made up to 200 cc.s. The solution, after being thoroughly mixed, is divided into two equal portions, each containing the bases in 1·2 gramme of slag. In one portion the lime and magnesia are determined in the filtrate from a double precipitation of the oxide of iron and alumina; the manganese being separated as sulphide by fractional filtration, and the results calculated on one gramme of slag, as in the case of an iron ore,

FeO.—The precipitate of oxide of iron and alumina obtained as described in the last paragraph is re-dissolved in *HCl*. The solution and washings, when cold, are made up to 120 cc.s, 100 cc.s, corresponding to 1 gramme of slag, are filtered off, neutralized, reduced, and the iron is determined by titration with standard bichromate solution, as in the case of an iron ore. The cc.s required are divided by 2, and the result $\times$ 1·2857 = % *FeO*.

Al_2O_3.—In the other 100 cc.s of the filtrate from the SiO_2, the Al_2O_3 is determined as phosphate, as in the case of an iron ore.

Analysis of Tap Cinder.

The constituents of this slag are determined as if the material under examination were an iron ore. If necessary, the ferrous oxide and silica may be determined from a fusion with acid potassium sulphate.

Analysis of Basic Slag.

SiO_2.—1 gramme of the finely-divided slag is dissolved in aqua regia and evaporated to dryness. The dry mass is re-dissolved in a little *HCl* and water; the insoluble silica is filtered off, and estimated as usual.

P_2O_5.—The filtrate and washings from the silica are evaporated to low bulk, excess of ammonia is added, the resulting precipitate is *just* re-dissolved in strong HNO_3. The liquid is boiled, and 100 cc. of the nitric acid solution of ammonium molybdate are added. The liquid is then digested nearly at boiling till clear. The yellow precipitate

is filtered off, washed with 2 % HNO_3 till free from iron, etc., and is re-dissolved in ammonia; some ammonium chloride is also added, and the P_2O_5 is then precipitated in the strongly ammoniacal solution by means of magnesia mixture, and is estimated in the usual manner.

CaO and MgO.—The lime and magnesia are determined in a solution of 0·6 gramme of the slag, from which the SiO_2 has been separated by filtration after evaporation to dryness with aqua regia. The P_2O_5, Fe_2O_3, and Al_2O_3 are separated as usual by double precipitation with ammonia, the manganese is removed as sulphide by fractional filtration from the double filtrate from the Fe_2O_3, etc. (see p. 251). In the $\frac{5}{6}$ fraction, corresponding to 0·5 gramme of slag, the CaO and MgO are determined as usual by precipitation as oxalate and double phosphate respectively.

Al_2O_3.—The alumina is determined as phosphate from a HCl solution of 1·2 grammes of slag by the process described for iron ores. The final precipitate may be slightly contaminated with Cr_2O_3.

FeO and Fe_2O_3.—The oxides of iron are determined as in the case of an iron ore, working, however, upon 2·5 grammes of slag, the results obtained being of course divided by five.

MnO.—For the determination of the MnO 2½ grammes of slag are dissolved in HCl, evaporated to low bulk, and the HCl is expelled by boiling the solution with strong HNO_3. A concentrated solution of 2 grammes of Swedish iron in nitric acid is then added to the liquid, and the manganese is determined by the Ford and Williams process in the usual manner. The result obtained, corrected for the manganese in the Swedish iron, and multiplied by two = % Mn, which × 1·2909 = % MnO. (The above calculation refers to the standard bichromate solution and weight

of iron specified for the determination of manganese in steel.)

Sulphur.—The sulphur is determined exactly as in the case of steel by the aqua regia process. That existing as calcium sulphide may be determined by the volumetric lead acetate process described on p. 106 *et seq.*

CrO_3.—Basic open-hearth slags often contain one or two-tenths % of CrO_3 derived from the chromite bricks used as an isolating course. To estimate it, 4 grammes of the slag are dissolved in HCl; the solution is boiled with 10 cc. of sulphurous acid, and then with 2 cc. of strong nitric acid. The solution is diluted, and the oxides of iron, aluminium, chromium, and phosphoric acid are thrown down by digesting with a slight excess of ammonia. The precipitate is filtered off, washed slightly, dissolved in hot dilute sulphuric acid, 1 in 4, and the chromium present is determined by Stead's volumetric method described on p. 157. If the standard solution of bichromate and the weight of iron there specified are used, each cc. left $= 0{\cdot}025$ % Cr, which $\times 1{\cdot}916 =$ % CrO_3. The result may be checked by fusing 2·4 grammes of the slag, and proceeding as for the estimation of chromium in steel by the gravimetric phosphate process, in carrying out which, however, no addition of sodium phosphate is required, the slag itself containing an ample quantity of P_2O_5.

Technical Analysis of Boiler Water.

Preparation of Standard Sodium Oleate (Soap) Solution (Tichborne).

$\frac{N}{1}$ (*Normal*) HCl.—Make a mixture of strong HCl solution and distilled water, placed in a tall cylinder, and

adjusted till the hydrometer indicates its sp. gr. to be 1·10; the solution will then contain about 20 % of true *HCl*. Counterpoise a beaker on the coarse balance and weigh out 181 grammes of the 20 % acid; transfer without loss to a litre flask, dilute to the mark with distilled water, and thoroughly mix. Ignite in a platinum dish at a moderate heat about 15 grammes of specially selected pure anhydrous Na_2CO_3. Cool in the desiccator, and weigh off into a 250 cc. graduated flask exactly 13·25 grammes of the carbonate. Dissolve in warm distilled water, and when cold dilute to the mark and thoroughly mix. Measure off 50 cc. into a 10 oz. flask, add about half a cc. of a strong solution of methyl orange, and from a burette run in the normal *HCl* solution, finally drop by drop, till the methyl orange changes to a much deeper tint, showing the alkali to be just neutralized. Thus—

$$Na_2CO_3 + 2\,HCl = 2\,NaCl + CO_2 + H_2O.$$
$$\begin{array}{ll} 106 & 73 \\ =53 & 36\cdot5 \end{array}$$

If the *HCl* solution is exactly normal just 50 cc. will be required, but probably such will not be the case, and it must be adjusted for weakness by the addition of 1·10 acid, or for strength by the addition of distilled water, in accordance with the principles explained on p. 89 in connection with the bichromate solution, till of exact normal strength.

Normal NaHO solution.—Weigh off in a platinum dish about 23 grammes of pure caustic soda from sodium metal. Transfer to a convenient porcelain dish, and dissolve in about 400 cc. of distilled water. When cold, transfer to a 500 cc. flask, dilute to the mark, and thoroughly mix. Measure off 50 cc. into a porcelain dish, and add a few drops of a solution of phenol-phthaleine in dilute alcohol, then run in the normal *HCl* solution till the last drop from

the burette just discharges the pink colour. If the sodic hydrate is normal just 50 cc. of acid will be required. The soda solution will, however, probably be too strong, and the number of cc. of distilled water necessary to bring it to normal strength are calculated, added, and the liquid is again checked with HCl to ensure its exact strength. Thus—

$$\underset{40}{NaHO} + \underset{36 \cdot 5}{HCl} = NaCl + H_2O$$

The alkaline liquid should be preserved in a green glass bottle provided with a well-fitting india-rubber stopper, and it is covered with a layer of pure light petroleum about $\frac{1}{8}$ in. thick, to prevent the absorption of CO_2 from the air. When required the solution is withdrawn from the bottom of the bottle by means of a pipette.

Standard soap solution.—Measure out into a beaker 5 cc. of pure oleic acid. Dissolve it in 50 cc. of proof spirit (equals approximately absolute alcohol 50 % + water 50 % by weight). Add a few drops of the phenol-phthaleine solution, and run in the normal $NaHO$ solution till the last drop just develops a permanent pink tinge. Thus—

$$\underset{\text{Oleic acid}}{HC_{18}H_{33}O_2} + NaHO = \underset{\text{Sodium oleate}}{NaC_{18}H_{33}O_2} + H_2O.$$

Let the number of cc. of $\frac{N}{1}$ soda required $= n$.

Then multiply n by 820 and divide by 15·5. The result gives the volume in cc. to which the solution must be diluted with proof spirit, so that each cc. of the somewhat turbid soap solution may be equal to 1 degree of hardness; that is to say, to 1 grain of $CaCO_3$ (chalk) per gallon when working upon 50 cc. of the sample of water to be tested. The correct strength of the liquid may be confirmed by a standard solution of pure $CaCO_3$ dissolved in

dilute HCl, evaporated to dryness and re-dissolved in water. 0·1429 gramme of $CaCO_3$ thus treated and dissolved in 1000 cc. of water = 10° of hardness, working on 50 cc. of the standard chalk solution.

Sampling.

For a technical analysis about one gallon of the water to be examined should be collected under average conditions in a clean, dry, stoppered Winchester quart. Suspended matter should not be separated, but before withdrawing the portions of the sample required for the various determinations the bottle should be thoroughly shaken.

Determinations of Total Hardness.

Measure off by means of a pipette into an 8-oz. narrow-mouthed bottle provided with a very well-fitting stopper 50 cc. of the water to be tested. Then run in from a burette the standard soap solution, half a cc. at a time, stoppering and violently shaking the bottle between each addition till a permanent lather is persistent, that is to say, when the bottle is laid on its side no bubble should be observed to break during a period of five minutes. The number of cc. of soap solution used, less 1 cc. (the amount necessary to produce a permanent lather in distilled water), give the degrees of hardness. These degrees are expressed in terms of 1 grain of $CaCO_3$ per gallon of water, but of course the hardness registered may be equivalently due to the presence of calcium sulphate or the sulphate or carbonate of magnesium. When the latter metal is

present the soiled white precipitate of oleates is very curdy in appearance. The reactions involved in the soap test may be exemplified thus—

$$\underset{\text{Sodium oleate}}{2\ NaC_{18}H_{33}O_2} + CaCO_3 = \underset{\text{Calcium oleate.}}{Ca\begin{cases}C_{18}H_{33}O_2\\C_{18}H_{33}O_2\end{cases}} + Na_2CO_3$$

When the hardness of the water exceeds 15 degrees, exactly 25 cc. of the sample are mixed with 25 cc. of distilled water, and the number of degrees registered is mulitplied by two. Should the hardness exceed 30 degrees, 10 cc. of the water are mixed with 40 cc. of distilled water, and the degrees then registered are multiplied by five.

Determination of Permanent Hardness.

Briskly boil for 1 hour 250 cc. of the water in an old frequently-used 30-oz. registered flask, marked with a slip of paper at 250 cc. Add distilled water from time to time to keep the volume of the liquid constantly about 250 cc. throughout the boiling. The flask and its contents are cooled, and a portion of the clear liquid is filtered off from the deposit, and is tested for hardness in exactly the same way as the original water. The number of degrees registered represent the permanent hardness, *i. e.* that due to $CaSO_4$ and $MgSO_4$, the boiling having driven off the CO_2 which held the $CaCO_3$ and $MgCO_3$ in solution as acid carbonates; the neutral carbonates are precipitated, leaving the permanently soluble sulphates in solution.

Determination of Temporary Hardness.

The total hardness − the permanent hardness = the temporary hardness.

Example.

Titration of a sample of hard water from the river Trent.

Total Hardness.—25 cc. of the river water + 25 cc. of distilled water required 15 cc. of standard soap solution.

$$(15 - 1) \times 2 = 28° \text{ of total hardness.}$$

Permanent Hardness.—The water was boiled for an hour, and when cold the precipitate was filtered off.

25 cc. of the boiled water + 25 cc. of distilled water required 12·5 cc. of soap solution.

$$(12{\cdot}5 - 1) \times 2 = 23° \text{ of permanent hardness.}$$

Temporary Hardness.—Total hardness = 28° 0

Total hardness		= 28° 0
Permanent	„	= 23° 0
Temporary	„	5° 0

Estimation of Total Solids.

Clean, gently ignite, cool and weigh a large platinum dish, and in it evaporate to dryness on the water-bath a carefully measured litre of the sample, introduced about 50 cc. at a time as the water evaporates. The litre-flask is well rinsed out with as little distilled water as possible, the washings are added to the dish, and the whole is taken to complete dryness, being finally heated for five minutes in the air-bath at 110°. The dish is allowed to go quite cold in the desiccator, and is quickly re-weighed. The increase = grammes of total solids in 1 litre of water: this multiplied by 70 = total solids in grains per gallon.

Estimation of Fixed Solids.

Place the dish on a pipe-stem triangle supported on a tripod, and by means of a small Bunsen burner gently

ignite the contents of the dish till the volatile organic matter (together possibly with nitrous fumes resulting from the decomposition of nitrates) has burnt off. When the dish is cold, in order to re-carbonate any lime or magnesia from which the CO_2 has been driven off, saturate the residue with a few drops of a 10 % solution of pure ammonium carbonate. Gently dry the contents of the dish, and finally again ignite at a temperature just sufficient to volatilize the ammonium salts: cool and re-weigh the dish. The increase over the original weight or the loss from the second weighing gives the fixed solids in grammes per litre.

Calculation of Volatile Solids.

The total solids — the fixed solids = the volatile solids in grammes per litre.

Analysis of the Fixed Residue.

CO_2.—Transfer about one-third of the residue from the platinum dish into the flask of the apparatus sketched in Fig. 4, and determine the CO_2 in the manner described for iron ores on p. 255.[1]

SO_3.—The residue remaining in the dish, the weight of which must be carefully noted, is dissolved by heating with a little moderately dilute *HCl*, and the solution is transferred, being, if necessary, filtered, without loss into a graduated 100 cc. flask, and when cold is diluted to the

[1] The weighing is best made by re-weighing the platinum dish after transferring approximately the portion specified to the flask; the loss = the weight taken.

mark and thoroughly mixed. It is then divided into two equal portions of 50 cc. each. In one the SO_3 is determined as $BaSO_4$ in the usual manner by boiling with an excess of $BaCl_2$.

CaO and MgO.—In the other 50 cc. of solution the lime and magnesia are precipitated respectively as oxalate and double phosphate in the manner described for iron ores. Any iron present may be determined in the usual manner in the ammonia precipitate by titration with the dilute solution of $K_2Cr_2O_7$ specified on p. 277.

Example.

Analysis of a sample of somewhat hard river water.
Volume taken for anlysis 1000 cc.

Weight of dish + total solids = 55·6239
Weight of dish = 55·4190

·2049 gramme per litre.
70

Total solids 14·3530 grains per gallon.

Weight of dish + fixed solids = 55·4087
Weight of dish = 55·4190

·1897 gramme per litre.
70

13·2790 grains per gallon.

Total solids = 14·3430
Fixed solids = 13·2790

Volatile solids = 1·064 grains per gallon.

Analysis of Fixed Solids.

CO_2.—Weight of dish + fixed solids = 55·6087
After taking portion for CO_2 = 55·5432

·0655 gramme.

Weight of CO_2 obtained 0·0073 gramme.

Then if 0·0655 yield 0·0073

0·1897 „ x

$$x = \frac{\cdot 1897 \times \cdot 0073}{\cdot 0655} = 0\cdot 0211$$

$$\begin{array}{r} 70 \\ \hline 1\cdot 4770 \end{array}$$ grains of CO_2 per gallon.

SO_3.—Weight taken $= \frac{\cdot 1897 - \cdot 0655}{2} = 0\cdot 1242$ gramme.

Weight of $BaSO_4$ obtained $= 0\cdot 1267$ gramme.

Then $\frac{\cdot 1267 \times 34\cdot 35}{100} = 0\cdot 0435$ gramme SO_3.

Then $\frac{\cdot 1897 \times \cdot 0435}{\cdot 1242} = \cdot 0665$

$$\begin{array}{r} 70 \\ \hline 4\cdot 6550 \end{array}$$ grains SO_3 per gallon.

CaO.—Weight taken 0·1242.

Weight of *CaO* obtained = 0·0436 gramme.

$\frac{\cdot 1897 \times \cdot 0436}{\cdot 1242} = \cdot 0666$

$$\begin{array}{r} 70 \\ \hline 4\cdot 6620 \end{array}$$ grains *CaO* per gallon.

MgO.—Weight taken 0·1242 gramme.

Weight of $Mg_2P_2O_7$ obtained 0·0103 gramme.

$\frac{0\cdot 0103 \times 27\cdot 93}{100} = \cdot 0029$ gramme *MgO*.

Then $\frac{\cdot 1897 \times \cdot 0029}{\cdot 1242} = \cdot 0044$

$$\begin{array}{r} 70 \\ \hline \cdot 3080 \end{array}$$ grain *MngO* per gallon.

$$\text{Results} — \left.\begin{array}{r} SO_3 — 4\cdot 655 \\ CO_2 — 1\cdot 477 \\ CaO — 4\cdot 662 \\ MgO — 0\cdot 308 \end{array}\right\} \text{grains per gallon.}$$

Which within the limits of error calculate out to

$$\left.\begin{array}{r} CaSO_4 — 7\cdot 913 \\ CaCO_3 — 2\cdot 506 \\ MgCO_3 — 0\cdot 647 \\ \hline 11\cdot 066 \end{array}\right\} \text{grains per gallon.}$$

Thus out of about 13 grains of fixed solids per gallon of water 11 grains consisted of a mixture of sulphate of lime and the carbonates of lime and magnesia, all compounds certain to deposit crust or scale on the plates of the boiler in which such water is used.

Determination of Chlorine.

Chlorides in moderate quantities are not objectionable in boiler water. Their determination is therefore seldom necessary. If required they are easily estimated and reported in terms of $NaCl$ by the process described for the alkalies in fire-clays on p. 285. In the present case, however, the standard solution of nitrate of silver is made by dissolving 1·711 grammes of the pure dry neutral salt in 500 cc. of distilled water.

Then working in a small porcelain dish on 50 cc. of the sample of water to be tested, each cc. used corresponds to 1 grain Cl per gallon of water. The grains of chlorine multiplied by 1·6479 equal grains of $NaCl$ per gallon.

APPENDIX.

DETERMINATION OF THE SPECIFIC GRAVITY OF IRON OR STEEL.

THE metal of which it is desired to find the specific gravity should be in the form of a turned and polished bar about 2 in. long by 0·3 in. diameter, which will weigh about 20 grammes, and is of convenient size to introduce into an ordinary 50 cc. specific gravity bottle. The latter is filled with pure distilled water at a temperature of 15° C., which should also be the temperature inside the balance-case.

The Method.

First.—The bar of steel after lying in the balance-case for some little time is accurately weighed.

Second.—The bottle having been filled with the water, the stopper is inserted, and the whole is carefully wiped with a clean soft linen handkerchief, and is accurately weighed.

Third.—The stopper is then removed, the bar of steel cautiously introduced, taking care that no air-bubbles adhere to the metal; the stopper is replaced and the

bottle wiped as before. The weight of the bottle, water, and steel is then determined; the result is calculated as follows—

Let s = the specific gravity @ 15° C.
" x = the weight of the metal in air.
" y = " " (bottle full of water) + (the weight of the steel in air).
" z = " " bottle, water, and metal.

$$\text{Then } s = \frac{x}{y - z}$$

Example.

Weight of steel bar in air	= 19·7754	grammes	(= x)
" bottle + water	= 71·8480	"	
" bottle + water + steel	= 89·1053	"	(= z)
Then 19·7754 + 71·8480	= 91·6234	"	(= y)
— (bottle + water + steel	= 89·1053	"	
Weight of water displaced	= 2·5181		

$$\frac{19·7754}{2·5181} = 7·8514 = \text{specific gravity @ 15°.}$$

Determination of the Carbides existing in Steel. (Author and A. A. Read.)

To estimate the carbide of Fe_3C or double carbides of the iron with manganese, chromium, etc., weighed polished bars of the steel 3 in. long by $\frac{3}{8}$ in. diameter are galvanically decomposed (by a modification of the method proposed by Binks and Weyl for the estimation of carbon in iron) in pure dilute HCl, sp. gr. 1·02, in the apparatus sketched in Fig. 21. The 40-oz. beaker A containing the dilute acid is provided with a porous cell and platinum plate, the latter being attached to the screw terminal B, which is connected with a zinc pole of a pair of pint Daniell cells, well charged in the shelf with $CuSO_4$ crystals. The bar is suspended at the pole C, 2 in. being immersed in the acid, which is attached to the copper terminal of the cells; D is a well-fitting cardboard disc to

prevent any copper salt (dissolved from the binding screw by the acid fumes) running down the bar. The circuit having been completed a stream of ferrous chloride (together in special steels with the chlorides of manganese,

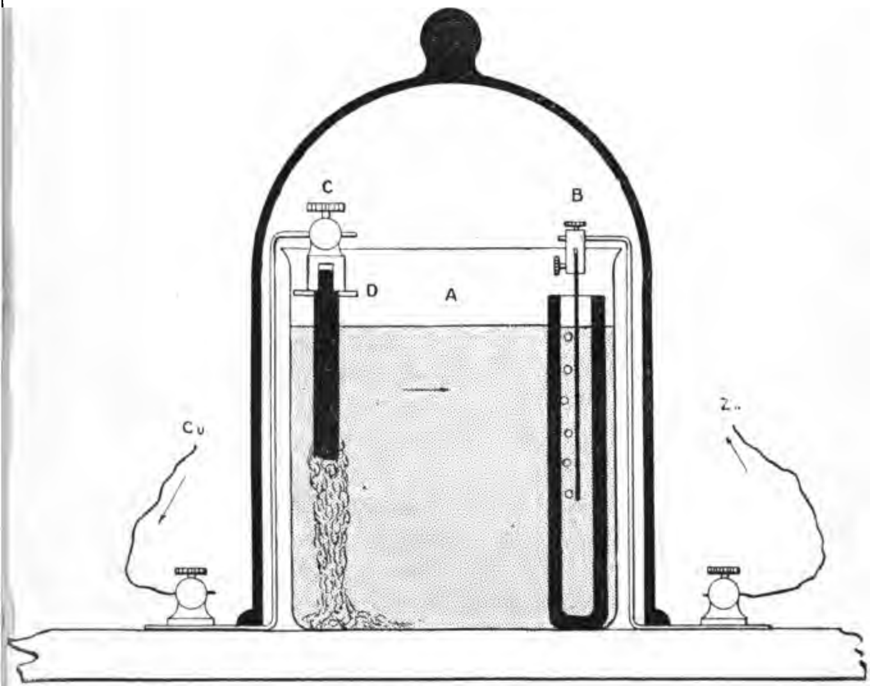


FIG. 21.

nickel, etc.) falls through the liquid, and hydrogen is briskly evolved at the platinum plate. In from six to twelve hours the bar is removed, and if it contains any considerable quantity of carbon it will be unaltered in shape but dark in colour (where it was immersed in the

acid), with an insoluble residue of the stable carbides present. The latter are scraped off with a clean blunt penknife, and are collected without loss on a small hardened filter-paper, the bar being finally well cleaned with a policeman. The residual metal is then wiped, dried, and re-weighed, the loss indicating the weight taken for analysis. The carbide residue is well washed with water containing a very little sulphurous acid, then with absolute alcohol, and finally with pure ether. It is then as far as possible transferred from the spread-out filter-paper to a weighed porcelain boat, first by means of a penknife, and then with a fine jet of ether. (The filter-paper to which a very small quantity of carbide adheres is burnt, the residual oxide weighed, and the iron in it calculated to carbide in accordance with the analysis of the main quantity.) The porcelain boat containing the carbide and ether is placed over strong sulphuric acid in a desiccator, till in about half-an-hour the ether has evaporated. The carbide is then dried *in vacuo* at 100° C. for two hours. This operation is simply carried out by boring two holes, about 1½ in. diameter, and exactly opposite each other, through the sides and near the bottom of a deep water-bath. Through these holes, made water-tight by good india-rubber bungs, is passed a glass tube about ¾ in. diameter inside, and attached at one end to a Spreugel pump, being closed at the other by means of an india-rubber bung carrying a tap and capillary tube. The boat containing the carbide having been inserted so as to lie in the middle of the bath, the tube is closed and the pump worked till a vacuum is obtained. The bath is then charged with water so as to well cover the tube, and is brought to boiling by means of a Bunsen burner. After about two hours, during which the action of the pump is

maintained, the lamp is removed, and the hot water taken out and replaced by cold. When the tube is cool air is very cautiously admitted through the capillary tube; the boat is taken out, cooled in the desiccator, and re-weighed, the increase giving the weight of carbide. The amount of carbon present is determined by strongly igniting the boat in a porcelain tube containing a column of copper oxide scales, the CO_2 being determined as in an estimation of carbon by combustion in steel. The residual oxide of iron is gently dissolved out of the boat in a flask containing strong nearly boiling HCl, is neutralized with ammonia, reduced with sulphurous acid, acidified with sulphuric acid, and the amount of iron present is determined by very careful titration with a standard bichromate solution of suitable strength. (Before titrating great care must be taken to boil off every trace of SO_2.)

In the case of double carbides the solution of the residue is divided into two parts, the iron being determined in one portion and the other elements in the second portion by the ordinary methods.

The carbon in the carbide obtained may equal from 70 to 96 % of the total carbon in the steel. The loss is due to the formation of liquid and gaseous hydrocarbons at the anode, a slight evolution of gas being almost invariably observed from the bar. Whether the loss is due to a very partial decomposition of the normal carbide, or to the existence of a readily decomposed sub-carbide, is not yet certain, but the evidence extant favours the latter view (see *Journal of the Chem. Soc.*, August 1894).

The carbide obtained from steels in an ordinary condition is a dark grey powder; that isolated from well-annealed steels exists in the form of bright silvery plates both varieties, however, correspond to the formula Fe_3C.

Example.

Determination of Fe_3C in a well-annealed crucible cast chisel steel containing 0·96 % of carbon. (Determined from the mean of two very closely agreeing combustions.)

Weight of bar before immersion	47·9828
,, ,, after ,,	41·5670
Loss = Weight taken	6·4158

Carbide all attached to the bar, and when dry presented the appearance of a somewhat coarse powder made up of minute silvery plates.

Weight of boat + carbide =	12·4386
Weight of boat =	11·5549
Weight of carbide obtained =	·8837

Weight of CO_2 obtained on combustion = 0·2126
= 0·05797 gramme carbon.

Weight of iron found in residue by titration = 0·816 gramme *Fe*.
Fe_2O_3 + filter ash = 0·0120
ash = 0·0007
0·0113 gramme Fe_2O_3 = 0·0079 gramme *Fe*.

$$\text{Then } \frac{\cdot0079 \times 6\cdot67}{93\cdot33} = 0\cdot00056 \text{ gramme carbon on filter.}$$

				Found.	Theory.
Total *Fe* = 0·8160 + 0·0079	= 0·82390	=	93·37 % *Fe*	93·33
,, *C* = 0·05797 + 0·00056	= 0·05853	=	6·63 % *C*	6·67
·88243				

Total residue = 0·8942 (= residue in boat + residue on filter).
Iron and Carbon = 0·8824
·0118 gramme impurity.

Analysis of Total Residue.

Carbide of iron Fe_3C = 98·68 } %
Impurities (SiO_2, H_2O, etc.) = 1·32 } %

$$\text{Total carbon in steel taken} = \frac{6\cdot4158 \times \cdot96}{100} = 0\cdot0606 \text{ gramme.}$$

Total carbon = 0·06060
Carbon in carbide = 0·05853
0·00207 gramme lost.

$$\text{Then } \frac{0\cdot05853 \times 100}{0\cdot0606} = 96\cdot58\ \% \text{ of total carbon obtained as } Fe^3C.$$

Therefore loss of total carbon as hydrocarbons and from errors of analysis = 3·42 %.

The foregoing example is an exceptionally satisfactory determination. The micro-section of the steel when examined at 600 diameters revealed the fact that the carbide had very beautifully crystallized out in innumerable definite and well-formed plates.

Experimental Determination of the Evaporative Power of Coal (Lewis Thompson).

The evaporative power of coal may be approximately determined in the laboratory by means of the apparatus shown in section in Fig. 22. This calorimeter consists of a capacious glass cylinder marked to contain when about two-thirds full of water at 60° F., 29010 grains; a copper tube or furnace fitting into a recess in a perforated stand, over the spring clips of which fits the combustion chamber, the latter consisting of a copper cylinder perforated round the edge of the open bottom end, and having a long pipe provided with a stop-cock at the closed top end. There is also a suitable thermometer for reading off the temperatures to $\frac{1}{5}$ of a degree F. With the apparatus is also supplied a second broad shallow furnace tube for burning coke or anthracite coal. The mixture used for burning the fuel is composed of 3 parts by weight of pure $KClO_3$, and 1 part by weight of pure KNO_3, both salts being very finely divided, intimately mixed, and dried at 100° C. before using. Of this mixture ordinary coal requires 300 grains, but coke and anthracite coal require 360 grains to completely burn 30 grains of the very finely-divided fuel dried at 100° C.

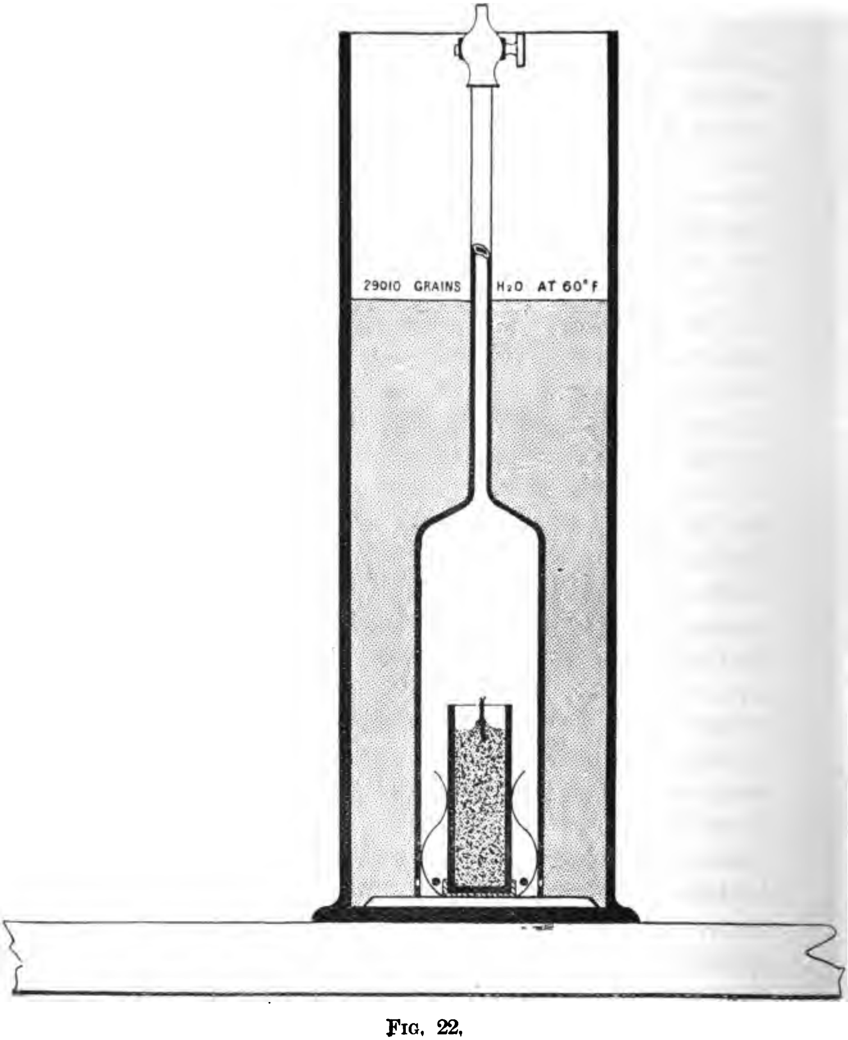


FIG. 22.

The Process.

The 30 grains of dry coal and the 300 grains of dry combustion mixture are very intimately incorporated by means of a clean palate knife on a sheet of stout glazed paper. The mass is transferred without loss to the copper furnace tube. After gently tapping the mixture down, a little hole about half-an-inch deep is made in it with a pointed wire, and into the cavity is inserted a little piece of rolled-up fuse (made by soaking strands of cotton wick in a solution of KNO_3 and allowing them to dry spontaneously) about one inch long, the mixture being packed round the fuse so that it (the fuse) projects about half-an-inch above the surface. The furnace tube is placed in the recess of the base-piece, the fuse is carefully ignited with a taper, and the combustion chamber, the tap of which must be shut, is *quickly* forced over the springs, and the whole is lowered into the glass cylinder previously accurately filled to the mark with water, the temperature of which was accurately noted. As soon as the fuse fires the combustible mixture, the elements of the coal are burnt to water and carbon dioxide by the oxygen contained in the chlorate and nitrate of potash. The steam formed is condensed, but the CO_2 and excess of oxygen violently bubble through the water, which absorbs their heat. The gases leave the water in the form of copious white fumes, due to the presence of finely-divided alkaline salts in a peculiar physical condition in which they escape being dissolved by the water. As soon as the combustion is over, the stop-cock is opened to allow the water to rise into the combustion chamber so as to take up the heat from the furnace tube. The thermometer is then put back into the cylinder, and

the copper portion of the apparatus is bodily raised and lowered in the water two or three times so as to render the temperature of the mass even throughout; the reading of the thermometer is then noted.

Example.

30 grains of a sample of coal suitable for making ordinary producer gas were intimately mixed with 225 grains of $KClO_3$ and 75 grains of KNO_3, and burnt as just described.

Temperature of water after combustion	70°·6
" " before "	58°·4
Difference	12·2
+ 10 %	1·22
One pound of coal evaporates	13·42 lbs. water.

That is to say, 1 lb. of coal converts 13·4 lbs. of water at a temperature of 212° F. into steam.

The 10 % added to the actual reading is a correction for the heat absorbed by the apparatus, which is set to this standard amount by the maker of the instrument.

Theoretical Considerations.

The capacity of the water cylinder is set in terms of the weight of fuel used and the latent heat of steam: thus, the latent heat of steam in British units is 967, and $967 \times 30 = 29{,}010$. In other words, each grain of fuel burnt has ready 967 grains of water to absorb the heat it has produced. In the example given, 1 part by weight of fuel has heated 967 parts by weight of water 13·4° F., which is equivalent to converting 13·4 lbs. of water at 212° into steam at 212°.

Theoretical Calculation of the Calorific Power and Intensity of Producer Gas from its Volumetric Analysis.

Convert the percentage composition by volume into percentage composition by weight. Example—

Let the percentage composition of a gas by volume be

$$\left.\begin{array}{lll} H & \text{Hydrogen} & 15 \\ CO & \text{Carbonic oxide} & 17 \\ CH_4 & \text{Marsh gas} & 7 \\ CO_2 & \text{Carbonic acid} & 6 \\ N & \text{Nitrogen} & 55 \end{array}\right\} \%\ \text{by volume.}$$

First find the weight in grammes of each constituent in 100 cc. of the gas at 0° and 760 mm. pressure.

Data.

$$\left.\begin{array}{ll} \text{cc.} & \\ 1000\ H & = 0{\cdot}0896 \text{ gramme.} \\ \text{,,}\ \ CO & = (\cdot 0896 \times 14) = 1{\cdot}2544 \\ \text{,,}\ \ CH_4 & = (\cdot 0896 \times 8) = 0{\cdot}7168 \\ \text{,,}\ \ CO_2 & = (\cdot 0896 \times 22) = 1{\cdot}9712 \\ \text{,,}\ \ N & = (\cdot 0896 \times 14) = 1{\cdot}2544 \end{array}\right\} \text{Grammes @ 0° C. and 760 mm. barometer pressure.}$$

Then—

$$15 \text{ cc. } H = \frac{\overset{\text{cc.}}{15} \times \overset{\text{grams.}}{\cdot 0896}}{\underset{1000}{\text{cc.}}} = 0{\cdot}0013440 \text{ gramme } H.$$

$$17 \text{ cc. } CO = \frac{17 \times 1{\cdot}2544}{1000} = 0{\cdot}0213248 \quad \text{,,} \quad CO.$$

$$7 \text{ cc. } CH_4 = \frac{7 \times 0{\cdot}7168}{1000} = 0{\cdot}0050176 \quad \text{,,} \quad CH_4.$$

$$6 \text{ cc. } O_2 = \frac{6 \times 1{\cdot}9712}{1000} = 0{\cdot}0118272 \quad \text{,,} \quad CO_2.$$

$$55 \text{ cc. } N = \frac{55 \times 1{\cdot}2544}{1000} = \underline{0{\cdot}0689920} \quad \text{,,} \quad N.$$

100 cc. of gas @ 0° C. and 760 mm. = 0·1085056 gramme.

Then—

$$\frac{\overset{\text{grammes}}{0 \cdot 001344} \times \overset{\%}{100}}{\underset{0 \cdot 1085056}{\text{grammes}}} = \overset{\%\text{ by weight.}}{1 \cdot 24\ H.}$$

$$\frac{2 \cdot 13248}{0 \cdot 1085056} = 19 \cdot 65\ CO.$$

$$\frac{0 \cdot 50176}{0 \cdot 1085056} = 4 \cdot 63\ CH_4.$$

$$\frac{1 \cdot 18272}{0 \cdot 1085056} = 10 \cdot 90\ CO_2.$$

$$\frac{6 \cdot 89920}{0 \cdot 1085056} = 63 \cdot 58\ N.$$

$$100 \cdot 00$$

The calculation is then made as in the case of the following example of coal, only in the present instance the volume of nitrogen in the gas must be included with that introduced from the air. The following additional data will also be required.

Calorific Powers.	Metric Units.	British Units.
CO	2403	4325
CH_4	13063	23513

Example of the Theoretical Determination of the Calorific Power and the Calorific Intensity of a Compound Fuel.

PROBLEM.

Assuming an initial temperature of 0° C., and ignoring sulphur and nitrogen,[1] calculate (in gramme units) the total heat and (in degrees Centigrade) the sensible temperature resulting from the combustion in air of 1 gramme of Welsh anthracite coal having the following percentage composition:—

Carbon	91·44
Hydrogen	3·46
Oxygen	2·58
Nitrogen	0·24
Sulphur	0·76
Ash	1·52
	100·00

[1] The exact reactions of these elements during the combustion are not known, but in any case their influence upon the results would be very small.

NECESSARY DATA.

Atomic Weights.	Reactions.	Specific Heats.	
$H = 1$	$2H + O = H_2O$	Water ...	$H_2O = 1{\cdot}000$
$C = 12$	2 16 18	Steam ...	$H_2O = 0{\cdot}480$
$O = 16$	$C + 2O = CO_2$	Nitrogen ...	$N = 0{\cdot}244$
	12 32 44	Carbon dioxide	$CO_2 = 0{\cdot}217$
		Ash ...	$= 0{\cdot}200$

	Calorific Powers.	Latent Heat of Steam.
Carbon = 8080 units Hydrogen = 34462 ,,	= Grammes of water raised through 1° C. by the heat of the combustion in oxygen of 1 gram. of the element.	537 grammes Centigrade units.

Composition of Air by weight.

Nitrogen...77 } Per cent.
Oxygen ...23 }

METHOD OF CALCULATION.

Step 1.

Determine the Calorific Power.

Step 2.

Calculate the weights of carbon dioxide, nitrogen, steam and ash resulting from the combustion of 1 gramme of the coal; multiply these weights by the respective specific heats and add the results. The number thus obtained represents the heat units necessary to raise the products of combustion through 1°.

Step 3.

Multiply the total weight of steam by 589 = the latent heat of steam 537 + 52 units. The latter number is a correction necessary from the fact that during the passage from 0° to 100° water has a specific heat of 1 instead of 0·480 as assumed in Step 2. Consequently the units absorbed over and above those necessary to raise the water from 0° to 100° had its specific heat been 0·480 will be $(1 - 0{\cdot}480) \times 100 = 52$ units of heat per gram. of water.

Step 4.

Subtract from the Calorific Power the number obtained in Step 3. Divide the remainder by the number obtained in Step 2. The quotient is the Theoretical Calorific Intensity or Pyrometric Effect in Centrigrade degrees.

Let I = Calorific Intensity in degrees.

,, P = Total Calorific Power in units.

,, WH = Sum of numbers obtained on multiplying weights by specific heats.

,, L = Units rendered latent by water and steam (= total $H_2O \times 589$).

Then $I = \dfrac{P - L}{WH}$

DETAILS OF WORKING.

P is obtained as follows :—

$$\text{Available Hydrogen} = \% H - \frac{\% O}{8} = 3{\cdot}46 - \frac{2{\cdot}58}{8}$$

$$= 8{\cdot}46 - 0{\cdot}32 = 3{\cdot}14\,\% \text{ available hydrogen.}$$

One gramme of the coal therefore contains of elements useful for fuel :—

$$\left.\begin{array}{lll} \text{Carbon} & \ldots & 0{\cdot}9144 \\ \text{Hydrogen} & \ldots & 0{\cdot}0314 \end{array}\right\} \text{gramme.}$$

Therefore the heat units developed by the combustion of the carbon and hydrogen respectively will be :—

$$\left.\begin{array}{l} 0{\cdot}9144 \times 8080 = 7388 \\ 0{\cdot}0314 \times 34462 = 1082 \end{array}\right\} \text{units.}$$

$$\underline{\underline{8470}} = P$$

WH is calculated as under :—

		Grammes.	Specific Heat.	Units.
CO_2 produced	$= \frac{0{\cdot}9144 \times 44}{12} = \frac{0{\cdot}9144 \times 11}{3} =$	$3{\cdot}3528$	$\times {\cdot}217 =$	$0{\cdot}7267$
N ,,	$= \frac{3{\cdot}3528 - ({\cdot}9144) \times 77}{23} + \frac{({\cdot}0314 \times 8) \times 7}{23} =$	$9{\cdot}0043$	$\times {\cdot}244 =$	$2{\cdot}1970$
H_2O ,,	$= {\cdot}0346 \times 9 =$	$0{\cdot}3114$	$\times {\cdot}480 =$	$0{\cdot}1495$
Ash ,,	$=$	$0{\cdot}0152$	$\times {\cdot}200 =$	$0{\cdot}0030$
		$12{\cdot}6837$		$3{\cdot}0071 = WH.$

L is found thus :—

$$0{\cdot}3114 \times 589 = 183 \text{ units} = L.$$

Then applying the formula *I* is obtained.

$$I = \frac{8470 - 183}{3{\cdot}0071} = \frac{8287}{3{\cdot}0071} = 2693^\circ \text{ C.}$$

The coal has thus a

Calorific Power of 8470 units and a
,, Intensity ,, 2693 degrees. Answer.

THEORETICAL CONSIDERATIONS.

A consideration of the following facts will assist to render the above operations clear :—

The temperature of a mass equals the number of sensible heat units in it divided by the product of its weight multiplied by its specific heat.

Thus if the 8287 sensible units present in the products of combustion could be absorbed (without giving up the 183 latent units also present) into 1 gramme of a body of specific heat 1, the temperature would be $\frac{8287}{1 \times 1} = 8287^\circ$.

But the actual weight of mixed matter yielded by the perfect combustion of the gramme of coal is 12·6837 grammes; and through this mass (the mean specific heat of which will be $\frac{3{\cdot}0771}{12{\cdot}6837} = 0{\cdot}2426$) has to be distributed 8287 units of heat. Hence the temperature or calorific intensity =

$$\frac{8287}{(12{\cdot}6837 \times 0{\cdot}2426)} = \frac{8287}{3{\cdot}0771} = 2693^\circ \text{ as before.}$$

NOTE.

Theoretical temperatures thus calculated give only the comparative values of fuels, and are considerably in excess of the temperatures obtained in practice. This is due mainly to the fact that the calculations are based upon three erroneous premises, viz.:—

1st.—It is assumed that the combustion of the fuel is perfect, whereas a variable portion escapes as finely-divided carbon (smoke), hydrocarbons, and carbonic oxide CO.

2nd.—It is assumed that only sufficient air enters a furnace to just effect the combustion, whereas in practice that entering the fire is in excess of the quantity required theoretically, and the variable surplus of air absorbs an amount of heat dependent upon its weight.

3rd.—It is assumed that the specific heat of the products of combustion is the same as at the ordinary temperature, whereas it is known that their capacity for heat increases with the temperature, but to what extent cannot be ascertained at furnace heats.

EXPRESSION OF RESULTS IN BRITISH UNITS.

To make the foregoing calculations in British units (lbs. of water raised 1° F.) and degrees Fahrenheit, the following data are substituted to obtain the Calorific Power and Intensity of 1 lb. of the coal:—

CALORIFIC POWERS.

$$\left.\begin{array}{ll}\text{Hydrogen} \ldots & 62032 \\ \text{Carbon} \ldots & 14544\end{array}\right\} \text{units} = \begin{array}{c}\text{lbs. of water raised 1° F. by the combustion} \\ \text{in oxygen of 1 lb. of each element.}\end{array}$$

Latent Heat of Steam 967 units + diff. in Specific Heat from 32° to 212° = $967 + \{(1 - \cdot 480) \times 180\} = 967 + 94$ units $= 1061$ units. This number multiplied by total $H_2O = L$.

TABLES OF TYPICAL ANALYSES.

TABLE I.—METALS.

Material.	Combined Carbon.	Graphite.	Silicon.	Manganese.	Sulphur.	Phosphorus.	Tungsten.	Chromium.	Aluminium.	Iron.
Swedish Lancashire hearth-iron ...	0·05	—	0·02	0·07	0·01	0·02	—	—	—	99·83
Cemented bar-iron and shear steel ...	0·95	—	0·02	0·07	0·01	0·02	—	—	—	98·93
Best English wrought iron	0·12	—	0·23	0·07	0·04	0·23	—	—	—	99·11
Best crucible chisel steel ("killed") ...	0·95	—	0·13	0·37	0·03	0·02	—	—	—	98·50
,, ,, ,, ,, (*Al* process) ...	1·00	—	0·04	0·05	0·02	0·02	—	—	0·02	98·85
Crucible turning-tool steel (2nd quality)	1·32	—	0·09	0·23	0·05	0·04	—	—	—	98·27
Self-hardening steel	1·65	—	0·63	1·82	0·04	0·03	9·89	1·03	—	84·91
Swedish Bessemer spring-steel ...	0·70	—	0·05	0·32	0·01	0·03	—	—	—	98·88
Open-hearth boiler-plate steel	0·23	—	0·02	0·53	0·05	0·06	—	—	—	99·11
English Bessemer spring-steel	0·51	—	0·08	1·03	0·06	0·05	—	—	—	98·89
Best steel castings (*Si* process) ...	0·39	—	0·42	0·78	0·05	0·06	—	—	—	98·30
,, ,, ,, (*Al* process) ...	0·45	—	0·11	0·37	0·05	0·06	—	—	0·03	98·93
Swedish white-iron	3·86	0·12	0·15	0·29	0·02	0·03	—	—	—	95·53
Swedish Bessemer mottled-iron ...	1·93	2·15	1·23	2·96	0·01	0·03	—	—	—	91·69
No. 1 Bessemer hematite iron ...	0·46	3·42	2·48	0·46	0·04	0·05	—	—	—	93·49
Pig-iron for basic process	0·83	2·56	0·98	1·63	0·07	1·83	—	—	—	92·10
Ordinary foundry pig-iron	0·72	2·74	1·54	0·56	0·09	0·86	—	—	—	93·49
Spiegel	4·32	—	0·46	15·10	0·02	0·23	—	—	—	79·87
Ferro-manganese	6·85	—	0·73	79·24	0·01	0·26	—	—	—	12·91
Ferro-chrome	7·65	—	0·28	0·23	0·14	0·08	—	63·40	—	28·22
Ferro-silicon	0·20	1·46	14·85	0·34	0·08	0·12	—	—	—	82·95
Ferro-aluminium	1·86	0·16	1·23	0·58	0·12	0·34	—	—	9·62	86·09
Ferro-tungsten	2·16	—	0·33	1·16	0·08	0·07	33·80	—	—	62·40

TABLE II.—ORES.

Material.	Fe_2O_3.	FeO.	MnO_2.	MnO.	Al_2O_3.	Cr_2O_3.	WO_3.	CaO.	MgO.	SiO_2.	TiO_2.	CO_2.	P_2O_5.	S.	Combined Water.	Organic Matter.
Red Hematite	74·23	—	0·28	—	6·61	—	—	1·02	0·01	8·62	—	0·79	0·02	0·02	8·43	—
Brown Hematite ...	64·63	—	Trace	—	3·92	—	—	0·90	0·25	13·50	—	2·30	2·16	0·05	11·63	—
Magnetite[1]	59·19	25·82	—	0·94	1·30	—	—	1·60	2·31	3·22	—	3·02	Trace	Trace	0·21	Trace
Clay ironstone	—	36·30	—	1·67	4·63	—	—	8·86	1·06	7·95	—	31·20	0·80	0·23	2·83	4·10
Impure Bauxite (Belfast)	28·74	0·78	—	Trace	41·30	—	—	1·70	0·23	14·05	0·30	—	0·02	0·01	13·85	—
Chrome iron ore ...	—	15·68	—	—	14·86	42·20	—	0·86	15·10	7·03	—	—	0·07	0·13	2·71	0·32
Manganiferous iron ore[2]	48·57	—	29·47	3·46	3·32	—	—	2·00	1·05	10·80	—	1·55	0·05	0·04	6·20	—
Wolfram	—	19·20	—	4·86	0·26	—	71·30	0·39	—	2·76	—	—	—	—	—	—

[1] Personally sampled by the author in the workings of the celebrated Dannemora mine, Sweden.

[2] ZnO 2·90, BaO 0·64.

TABLE III.—REFRACTORY MATERIALS. (Dry.)

Materials.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	($x\,K_2O+$ $y\,Na_2O$).	Combined water.
Fire-clay	50·93	32·72	2·06	Trace	0·97	1·72	10·63
Fire-brick (Stannington)	64·03	29·48	3·60	0·21	0·99	1·53	—
Silica brick (Deepcar) ...	96·20	1·17	1·06	0·98	Trace	—	—
Ganister	95·32	1·26	0·86	Trace	Trace	—	1·72
Basic brick	1·86	0·84	1·30	58·65	36·70	—	—

TABLE IV.—FUELS. (Dried at 100° C.)

Material.	Coke.	Volatile matter.	Ash.	Sulphur.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
Brown coal ...	—	—	7·56	—	62·35	4·89	23·60	0·95
Bituminous coal	62·50	37·50	3·73	1·06	80·05	4·93	8·99	1·24
Coke	100·00	0·49	7·57	0·82	89·21	0·43	1·65	0·23
Charcoal ...	—	—	1·96	—	87·41	3·02	7·26	0·40

ANALYSIS OF COAL ASH.

SiO_2 42·75	Al_2O 26·20	Fe_2O_3 15·40	CaO 7·30	MgO 1·56	Alkalies 1·08	SO_3 5·26	P_2O_5 1·05

TABLE V.—SLAGS.

Material.	SiO_2.	CaO.	MgO.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	P_2O_5.	S.	Alkalies.
Blast furnace slag	36·80	43·50	1·63	14·64	—	0·95	2·35	0·02	0·62	1·27
Finery slag (ferrous silicate)	33·33	1·19	0·50	5·57	—	54·94	2·71	2·30	0·10	—
Acid Bessemer slag ...	47·90	1·35	0·56	3·98	—	15·20	31·60	Trace	Trace	—
Basic Bessemer slag ...	11·64	51·90	6·37	0·82	1·60	7·30	4·86	14·60	0·17	—
Tap cinder	14·60	3·16	0·27	2·56	15·20	55·69	1·25	5·60	1·98	—

TABLE VI.—TECHNICAL ANALYSES OF BOILER WATERS.

Class of water.	Solids in grains per gallon.			Hardness by soap test in degrees.[1]			Analyses of fixed solids in grains per gallon.			
	Total.	Volatile.	Fixed.	Total.	Temporary.	Permanent.	CO_2.	SO_3.	CaO.	MgO.
Very bad	53·78	5·42	48·36	36·5	2·0	34·5	0·98	25·92	19·30	0·35
Good	5·63	0·73	4·90	3·0	2·5	0·5	0·68	0·52	1·37	Trace

[1] Each degree is equivalent in hardness to one grain of $CaCO_3$ per gallon.

ATOMIC WEIGHTS OF THE MORE IMPORTANT ELEMENTS.

(Stated to the nearest first decimal.)

Element.	Symbol.	Atomic weight.	Element.	Symbol.	Atomic weight.
Aluminium ...	*Al*	27·3	Mercury ...	*Hg*	199·8
Antimony ...	*Sb*	122·0	Molybdenum	*Mo*	95·8
Arsenic ...	*As*	74·9	Niobium ...	*Nb*	94·0
Barium ...	*Ba*	136·8	Nickel ...	*Ni*	58·6
Bismuth ...	*Bi*	210·0	Nitrogen ...	*N*	14·0
Boron ...	*B*	11·0	Oxygen ...	*O*	16·0
Bromine ...	*Br*	79·6	Palladium ...	*Pd*	106·2
Cadmium ...	*Cd*	111·6	Phosphorus	*P*	31·0
Calcium ...	*Ca*	39·9	Platinum ...	*Pt*	196·7
Carbon ...	*C*	12·0	Potassium ...	*K*	39·0
Chlorine ...	*Cl*	35·4	Rhodium ...	*Rh*	104·1
Chromium ...	*Cr*	52·2	Selenium ...	*Se*	79·0
Cobalt ...	*Co*	58·6	Silver ...	*Ag*	107·7
Copper ...	*Cu*	63·1	Silicon ...	*Si*	28·0
Fluorine ...	*F*	19·1	Sodium ...	*Na*	23·0
Gold ...	*Au*	196·2	Strontium ...	*Sr*	87·2
Hydrogen ...	*H*	1·0	Sulphur ...	*S*	32·0
Iodine ...	*I*	126·5	Tin	*Sn*	117·8
Iridium ...	*Ir*	192·7	Titanium ...	*Ti*	48·0
Iron	*Fe*	55·9	Tungsten ...	*W*	183·5
Lead ...	*Pb*	206·4	Uranium ...	*U*	240·0
Lithium ...	*Li*	7·0	Vanadium ...	*V*	51·2
Magnesium ...	*Mg*	23·9	Zinc	*Zn*	64·9
Manganese ...	*Mn*	54·8			

TABLE OF THE PERCENTAGES OF ELEMENTS OR COMPOUNDS IN THE PRECIPITATES.

Formula of Precipitate.	Element or Compound required.	Percentage in Precipitate.
$AlPO_4$	Al	22·18
$AlPO_4$	Al_2O_3	53·00
$BaSO_4$	S	13·75
$BaSO_4$	SO_3	34·35
$CaSO_4$	CaO	41·20
CO_2	C	27·27
Cr_2O_3	Cr	68·48
$Cr_6P_4O_{19}$	Cr	42·48
$Cr_6P_4O_{19}$	Cr_2O_3	60·95
Fe_2O_3	Fe	70·00
$Mg_2As_2O_7$	As	48·30
$Mg_2As_2O_7$	As_2O_5	74·20
$Mg_2P_2O_7$	MgO	36·04
$Mg_2P_2O_7$	P	27·93
$Mg_2P_2O_7$	P_2O_5	63·96
Mn_3O_4	Mn	72·05
Mn_3O_4	Mo	93·01
Molybdic yellow ppt.	P	1·63
Molybdic yellow ppt.	P_2O_5	3·73
NiO	Ni	78·56
SiO_2	Si	46·67
TiO_2	Ti	60·00
WO_3	W	79·31

TABLE OF FACTORS.

Weight of	*Fe*	multiplied by	1·2857	=	*FeO*.
,,	*Fe*	,,	1·4288	=	Fe_2O_3
,,	*Cr*	,,	1·4600	=	Cr_2O_3
,,	*Mn*	,,	1·2909	=	*MnO*
,,	*Mn*	,,	1·5818	=	MnO_2
,,	Mn_3O_4	,,	0·9300	=	*MnO*
,,	*CaO*	,,	1·7846	=	$CaCO_3$
,,	*MgO*	,,	2·2150	=	$MgCO_3$

Comparison of English and Metric Weights and Measures.

Weights.

1 gramme	=	15·432348 grains.
1 grain	=	0·064792 grammes.
1 oz. troy	=	31·103496 grammes or 480·0 grains.
1 oz. avoir.	=	28·349540 grammes or 437·5 grains.

Lineal Measure.

1 inch	=	25·39954 millimetres.
1 millimetre	=	0·03937079 inches.

Square Measure.

1 square inch	=	645·13669 square millimetres.
1 square mm.	=	0·001550059 square inches.

Cubic Measure.

1 cc.	=	0·0610270734 cubic inches.
1 cubic inch	=	16·386 cubic centimetres.
1 cc.	=	0·0352754 fluid ounces.
1000 cc.	=	1·76077 pints or 0·2200967 gallon.
1 gallon	=	4543·458 cc.

To convert grammes per litre into grains per gallon multiply by 70.

Conversion of Thermometer Scales.

To convert degrees Centigrade into degrees Fahrenheit

$$\frac{°C. \times 9}{5} + 32 = °F.$$

To convert degrees Fahrenheit into degrees Centigrade

$$\frac{(°F. - 32) \times 5}{9} = °C.$$

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